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° AN INTRODUCTION
TO
QUALITATIVE
CHEMICAL ANALYSIS

BY
THE INDUCTIVE METHOD.

A LABORATORY MANUAL
FOR
COLLEGES AND HIGH SCHOOLS.

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PROFESSOR OF CHEMISTRY, ALBION COLLEGE.



LEACH, SHEWELL, & SANBORN,
BOSTON AND NEW YORK.

1895

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PREFATORY NOTE.

THIS manual is designed to impart but little chemical truth directly. It aims rather to lead the student to gain that truth himself as nearly as possible at first hand and as a product of his own thinking. This he is enabled to do, without waste of time, guided as he is by the suggestions of the book and the constant prevision of the live teacher.

The student is first thoroughly grounded in the fundamental ideas of chemistry before he goes on to use those ideas as tools in the practical work of qualitative analysis. If he gains a proper conception of the relation of the atom to the molecule, of valence; if he masters the principles of nomenclature and the chemical equation as set forth in chapters ii. and iii., he will certainly acquire his chemistry with facility and clearness. That it produces strong, accurate, enthusiastic, and independent students the author has demonstrated in his own classes through several years.

For the sake of emphasizing what is expressed elsewhere, the author would insist upon regular recitations, at stated times, upon the laboratory work, in which there shall be full and searching discussion of the results obtained, of errors committed, how these errors have arisen and how controlled. Comparison of results obtained and informal discussion of the difficulties to be met with beget an interest and enthusiasm for the work which is invaluable. Moreover, a few experiments fully reported and discussed are of much greater value than many experiments with little time given to such discussion.

ALBION COLLEGE,
September, 1892.
April, 1894.

TABLE OF CONTENTS.

	PAGE
Preface.	
Methods	I
The Plan	2
Time required	3
The Daily Program	3
The Student in the Laboratory	4
CHAPTER I. — Preliminary Definitions	7
Analysis, Synthesis, Atom, Molecule, Element, Compound, Mix- ture, Chemical Affinity, Chemical Action, Chemical Compounds, . Valency, Atomic Weight, Molecular Weight, Metal, Non-metal, Satisfied and Unsatisfied Compounds, Chemical Symbols	8
Table of Elements	9
Chemical Formulas, Oxides, Hydroxides, Acids, Salts	11
CHAPTER II. — Nomenclature	12
List of Acids and Formulas	12
Nomenclature of Acids: Oxacids, Hydracids, Exchangeable Hy- drogen, Acid Radical, Bibasic and Tribasic Acids	12
Nomenclature of Salts	13
Neutralization	13
Naming Salts, Writing Formulas	14
CHAPTER III. — The Laboratory	16
Chemicals and Apparatus, Inventory of Chemicals on Student's Table	17
Inventory of General Table	17
Apparatus for Student's Table	19
CHAPTER IV. — Solids and Liquids	22
To Change Solids into Liquids	22
To Change Liquids into Solids	24

	PAGE
CHAPTER V. — Chemical Equations	26
Method of Writing, Method of discussing	26-29
Practical Suggestions	30
Table of Solubilities	31
CHAPTER VI. — Grouping of the Metals	32
First Group of Metals	32
Second Group of Metals	33
Third Group of Metals	34
Fourth Group of Metals	35
Fifth Group of Metals	35
Table of Grouping of Metals	37
CHAPTER VII. — Separation of the Metals of First Group	38
Method of Separation	38
Confirmatory Tests	39
Synoptical View	40
CHAPTER VIII. — Occurrence in Nature of First Group Metals	41
CHAPTER IX. — Separation of Metals of Second Group	43
Method of Separation, Marsh's Test, Spot Tests	43-45
Specimen Pages from Student's Note Book	45
Confirmatory Tests	47
Synoptical View	48
CHAPTER X. — Occurrence in Nature of Second Group Metals	49
CHAPTER XI. — Separation of Metals of Third Group	51
Table Work	51
Questions on the Table Work	51
A Study in Oxidation	52
Tests for Fe, Cr, and Al	53
Tests for Mn, Zn, Co, Ni	54
Confirmatory Tests	54
Synoptical View	56
CHAPTER XII. — Occurrence in Nature and Uses of Third Group Metals	57
CHAPTER XIII. — Separation of Metals of Fourth Group	59
Table Work, Questions on	59
Confirmatory Tests	61
Synoptical View	62
CHAPTER XIV. — Occurrence and Uses of Fourth Group Metals	63
CHAPTER XV. — Separation of Metals of the Fifth Group	65
CHAPTER XVI. — Occurrence and Uses of Fifth Group Metals	67

CONTENTS.

vii

	PAGE
CHAPTER XVII. — The Periodic Law of the Elements . . .	69
CHAPTER XVIII. — Unknowns, Mixtures	71, 72
CHAPTER XIX. — Acids	74
Classification of Acids	74
Notes and Queries	75
Examination of Salts for Acids	75
Confirmatory Tests	76
CHAPTER XX. — Some Dry Processes	82
Flame Tests, on Charcoal, Borax Bead	82, 83
Care of Platinum vessels	83

PLANS AND METHODS OUTLINED.

LABORATORY practice, as often carried on, consists in setting before the student a task to perform, the end of which is known to him as well at the beginning of a series of experiments as at its close. He may see the fact more clearly, but the substance of the truth he knew to begin with. Recognizing this, he assumes at least an attitude of doubt as to the value of laboratory work. Especially is this true when he comes fresh from the study of history or language, where he has been trained to regard the printed page as the only authority obtainable or necessary.

The object sought in conducting the student through a course in qualitative chemistry by the method embodied in this book, is to counteract this tendency to undervalue laboratory work, and also to place him as nearly as possible, from the first, under the conditions enjoyed by the original investigator.

For example, a frequent method of procedure is to make the statement to the student that the reagent hydrochloric acid will only precipitate silver, lead, and mercurous salts. He seldom doubts this, and, acting on his previously acquired habit of regarding the printed statement as sufficient authority, he does not appreciate the desirability or necessity of demonstrating it. If he does proceed to investigate the question by practical tests, his work will, in many cases, consist in making the three precipitates in question, and perhaps trying the effect of the reagent on one or two additional salts. It will be seen that this is no demonstration whatever.

If, however, he should be sent to the laboratory with the

single question, "How does hydrochloric acid affect salts in solution when added to them?" it is clear he could not consider his work as completed until he had applied the acid to representative salts of at least all the more commonly occurring metals. When this was done, he would discover the fact that hydrochloric acid will precipitate silver, lead, and mercurous salts, and *no other*. An easy deduction from this work leads him to the capital truth that the reagent hydrochloric acid will separate salts of these metals from all others. He would then feel himself to be, and would be, quite as much the discoverer of the truth as the one who first came into possession of it.

It will be objected that it is wrong to oblige the student to pursue this work of discovering truths already well established; that he ought to enter into and take advantage of the fruits of previous toilers, and himself push out into fields not yet occupied. This is very true, but a great defect in the student's training will arise from the fact that his habits, his methods of study and investigation, are given him by his first lessons. If his initial lessons do not introduce him to the true scientific method it is doubtful whether he will appreciate it fully when set before him farther on in his course.

It will also be objected that this course will take more time than can ordinarily be given to this subject. In answer to this it may be urged that the teacher must not regard time when it weighs against false or true methods; that slowness at the start only makes progress more rapid when correct habits have been formed. This the writer has found to be true in his trial of this method through several years.

The Plan. — The plan may be described as a combination of (1) original investigation and (2) references to authorities.

In the beginning (1) will be a very small factor and (2) correspondingly large. As experience in manipulation, observation, and interpretation increases, (1) will increase and the necessary dependence on (2) will decrease. To the experi-

enced chemist (1) is very large and (2) very small; in other words, he is his own authority. See page 21.

Time Required.—Two terms of fourteen weeks each are thought to be sufficient to cover a course in general descriptive chemistry, and also lay a thorough foundation for a course in qualitative analysis. The non-metals may be studied from some general text-book, this occupying three or four fifths of the first term. The qualitative work may begin after the middle of the term, with one or two recitations per week, or this work may be deferred till the beginning of the second term. After the metals of a given group have been studied, the general text-book may again be used for answers to the questions under "Occurrence in Nature."

The Daily Program.—The advance work for each day will consist in finding, by actual tests in the laboratory, or by reference to proper authority, answers to the questions, making proper memoranda of all transactions, and writing equations for all cases of chemical action.

The class will then come together to make report of progress and for a mutual discussion by teacher and class of the details of the work, and especially of all deductions and truths which have been brought to light. Much time should be spent in the recitation room, tabulating and comparing results, discussing the work, and formulating principles.

While this discussion is in progress, the student should write out in full, by direct discourse, so much of the theory and practice of chemical analysis as his work has made clear to him.

The catechetical method is only employed where it is thought to be the clearest method to lead the learner to the truth; nor is it claimed that all the queries that ought to be started are here given. These are merely typical of many others that will spring up in the mind of the thoughtful student. That which is presented here is only the skeleton or framework; the body of truth must be built up by the united

efforts of the live and energetic teacher and the enthusiastic student. Indeed, it must be insisted that this book is not at all complete in itself; that the one claim it puts forward for originality lies in the fact that it continually compels the student to seek, by tests in the laboratory or in other books, the information he desires.

To the Student.

On entering a laboratory, whether physical, biological, or chemical, the student should thoroughly appreciate the changed relations and different surroundings in which he finds himself. He has studied literature, history, mathematics, language, or philosophy, in the privacy and quiet of his own room; he has studied from books, but, on taking up the study of the natural sciences, his books have been taken from him, and in their place he is given specimens and objects of natural history. He is led to look at these objects, observe as many characteristics as possible, make notes, arrange and classify the facts and truths thus obtained, draw his own conclusions, and discover underlying principles and laws.

Every true student will delight in discovering truth for himself, and in order to accomplish this he must early be taught the methods by which this appeal to first sources is made. No field presents better opportunities for this kind of study than chemistry.

Many difficulties lie in the way of such methods, and it is the student's first business to know what those difficulties are and conquer them as soon as possible.

(1) He studies in the laboratory in company with other members of his class, and this necessitates some confusion which distracts his attention from the work in hand. To learn to isolate himself from all others by becoming absorbed in his work is his first duty.

(2) His apparent progress at first will necessarily be somewhat slow. He must learn to appreciate the greater value of a

single truth acquired by himself than many learned at second-hand.

(3) The student naturally expects by this method to obtain only those facts which are made apparent to him through his physical senses. One of the early things which he must learn is that in the acquisition of truth he must enlist his whole being, sight, hearing, touch, etc. ; in a still greater degree there must be brought into action his reason, judgment, and imagination. All the powers of the mind and body must be so disciplined and trained that they can be concentrated upon the particular object of study.

(4) His memory must grasp and hold the whole of a series of facts until they can be brought into their proper relations and the principles and laws discovered which bind them together.

(5) He must be a diligent student of language in order that what he sees may be clearly described. Knowledge is of little value if for lack of power of expression it must forever be locked up in the mind of the one who discovered it.

(6) He must early learn that courage and persistence are needed if he would come into a clear apprehension of truth. He must be willing to do much of what has been denominated "dead work;" that is, work that has been done by others before him. Much of his work he must do over and over again, until, by familiarity with it, its true significance is brought to light.

This leads to the consideration of another question ; namely, Where shall a student's work stop ? It may stop at any one of several points, each denoting varying degrees of excellence in that work. For example, he may

(1) Be content to read a statement and simply give his assent to it.

(2) He may so memorize that statement as to be able to reproduce it when necessity requires.

(3) He may verify the truth by the observation and study of an appropriate experiment in the laboratory.

(4) To obtain a still more definite knowledge of the point in hand he may prepare abstracts, and illustrate by diagrams.

(5) He may obtain by any of these partial methods a conception of the truth, by which he is enabled to make a creditable recitation, provided he has help from his teacher, and the privilege of retracing his steps and thus amending his previous statement ; or,

(6) He may impose upon himself the highest and best test of the accuracy of the knowledge he has obtained, and his familiarity with it, by reducing that knowledge to a clear, concise, and original written statement which will withstand the criticism of others.

Some students, so-called, are content to stop at the first-mentioned point ; most students go as far as the second or third ; many faithfully practice the fourth, and strive to attain to the degree of excellence suggested by the fifth point. A notable and praiseworthy few are not satisfied with anything less than the accomplishment of the work contemplated in the sixth suggestion.

The author records it as his deliberate judgment, after years of experience, that in order that the greatest good shall be derived from the work which follows, the student must prepare a note-book covering the entire work. It may simply be supplemental to this book ; but a much better plan is to make it complete in itself, including title-page, a short introduction, preliminary definitions, laboratory memoranda, equations, tabulated work, synopses, and especially all facts and principles which have been deduced from the work. Nothing else can take the place of this part of the study.

QUALITATIVE CHEMICAL ANALYSIS.

CHAPTER I.

PRELIMINARY DEFINITIONS.

What is analysis? Synthesis?

What is chemical analysis?

What is organic analysis? Inorganic analysis?

What is qualitative analysis? Quantitative analysis?

What is volumetric analysis? Gravimetric analysis?

There are certain fundamental ideas and principles concerning the atom and molecule, and their relations to each other, which can not well be illustrated by simple experiments, and much less can they be demonstrated by this method. It is, however, very necessary to have them in mind as the work contemplated in the following pages is entered upon. These have largely been met and studied in the general chemistry which the student is supposed to have had preparatory to this course, and they are repeated here by way of review.

Answers to the following questions may be supplied by the teacher, or sought out in any reliable text-book on general chemistry.

What is an atom? A molecule? A simple molecule? A compound molecule?

What are elements? Compounds? Mixtures?

Perform the following experiments, and find illustrations of the above three terms.

1. Add carbon disulphide separately to some flowers of sulphur and iron powder and note the effects.
2. Try the effect of a magnet on each.
3. Thoroughly mix, with a pestle and mortar, seven parts by weight of the iron and four parts of the sulphur.
4. Repeat experiments 1 and 2 on the substance in the mortar.
5. Fill a dry test-tube one-third full with the substance from the mortar, and strongly heat the lower end.
6. After fusion has taken place, and the substance has cooled, repeat experiments 1 and 2.

Define chemical affinity ; chemical action ; chemical work.

Atoms when apart possess *chemical affinity* or chemical energy. This energy may be thought of as the variety called potential ; when this is transformed into kinetic energy, or energy of motion, *chemical action* takes place ; the work done or result produced is a *chemical compound*.

What is understood by atomic weight ? By molecular weight ?

What is a metal ? A non-metal ?

In the decomposition of compounds by the electric current it is found that invariably hydrogen and the metals seek the negative pole of the battery, while the non-metals are found at the positive pole. In this electrical behavior of the chemical elements there is a possible explanation, by analogy at least, of the fact that the strongest chemical affinity exists when a metal is brought near to a non-metal, the latter elements having only a secondary attraction for each other, and the metals scarcely ever uniting together. In the great majority of cases, therefore, chemical compounds contain both metals and non-metals.

TABLE OF 70 ELEMENTS.

This table represents trustworthy results, reduced to a uniform basis of comparison, with Oxygen = 16 as a starting-point of the system. No decimal places representing large uncertainties are used. When values vary, with equal probability on both sides, so far as our present knowledge goes, as in the case of cadmium (111.3 and 112.2), the mean value is given in the table.

NAME.	SYMBOL.	ATOMIC WEIGHT.	VALENCE.	NAME.	SYMBOL.	ATOMIC WEIGHT.	VALENCE.
Aluminum ..	Al	27.	II, III	Neodymium ³ ..	Nd	140.5	-
Antimony	Sb	120.	III, V.	Nickel	Ni	58.7	II, IV.
Arsenic	As	75.	III, IV.	Nitrogen	N	14.03	(I), III, IV.
Barium	Ba	137.	II.	Osmium	Os	197.7	-
Bismuth	Bi	208.9	III, V.	Oxygen ⁴	O	16.	II.
Boron	B	11.	III.	Palladium	Pd	106.6	-
Bromine	Br	79.95	I. (V).	Phosphorus ...	P	31.	(I), III, V.
Cadmium	Cd	112.	II.	Platinum	Pt	195.	(II), IV.
Cæsium	Cs	132.9	-	Potassium	K	39.11	I.
Calcium	Ca	40.	II.	Praseodymium ³	Pr	143.5	-
Carbon	C	12.	(II), IV.	Rhodium	Rh	103.5	-
Cerium	Ce	140.2	-	Rubidium	Rb	85.5	-
Chlorine	Cl	35.45	I, V.	Ruthenium ...	Ru	101.6	-
Chromium ...	Cr	52.1	(II), III.	Samarium	Sm	150.	-
Cobalt	Co	59.	II, IV.	Scandium	Sc	44.	-
Columbium ¹).	Cb	94.	-	Selenium	Se	79.	II.
Copper	Cu	63.4	I, II.	Silicon	Si	28.4	IV.
Erbium	Er	166.3	-	Silver	Ag	107.92	I.
Fluorine	F	19.	I, (V).	Sodium	Na	23.5	I.
Gallium	Ga	69.	-	Strontium	Sr	87.6	II.
Germanium ...	Ge	72.3	-	Sulphur	S	32.06	II, IV, (VI).
Glucinum ²)	Gl	9.	-	Tantalum	Ta	182.6	-
Gold	Au	197.3	III.	Tellurium	Te	125.	-
Hydrogen	H	1.007	I.	Terbium	Tb	159.5	-
Indium	In	113.7	-	Thallium	Tl	204.18	-
Iodine	I	126.85	I, (V).	Thorium	Th	232.6	-
Iridium	Ir	193.1	-	Tin	Sn	119.	II, IV.
Iron	Fe	56.	II, III.	Titanium	Ti	48.	-
Lanthanum ...	La	138.2	-	Tungsten	W	184.	-
Lead	Pb	206.95	II, IV.	Uranium	U	239.6	-
Lithium	Li	7.02	I.	Vanadium	V	51.4	-
Magnesium ...	Mg	24.3	II.	Ytterbium	Yb	173.	-
Manganese ...	Mn	55.	II, IV, VI.	Yttrium	Yt	89.1	-
Mercury	Hg	200.	I, II.	Zinc	Zn	65.3	II.
Molybdenum.	Mo	96.	-	Zirconium	Zr	90.6	-

1) Or Niobium.

2) Or Beryllium.

3) Didymium now split into Neo- and Praseo-Didymium.

4) Standard, or basis of the system.

What is a saturated compound? An unsaturated compound?

What kind of compounds are capable of entering into chemical action without being first decomposed?

NOTE.—The theories involved in the foregoing questions are very complex, and it is not expected that they will be perfectly clear to the mind of the beginner; but their constant use and universal application to all chemical problems will gradually bring their deep significance into view.

What are chemical symbols?

What are chemical formulas? Give illustrations.

NOTE.—The Quantitative Chemist first learns what the chemical formula of a certain substance is, and the Qualitative Chemist accepts his authority and follows it.

What is meant by valence?

What is a univalent element? A bivalent element? A trivalent element? A quadrivalent element?

What is a monad? A diad? A triad? A tetrad?

When is an element said to have "one bond"? "Two bonds"? "Three bonds"? etc.

How may the valence of an element oftentimes be observed from a formula?

What is the valence of Cl in HCl ? Sb in SbCl_3 ? Mg in MgSO_4 ? Fe in $\text{Fe}_2(\text{SO}_4)_3$? SO_4 in H_2SO_4 ? K in KCl ? PO_4 in K_3PO_4 ? O in H_2O ? C in CO_2 ?

What is the water of crystallization? When should this be taken into account and included in the formula?

Take a piece of glass tubing 20 cm. long; soften the middle point in the flame, and draw the two halves apart, thus making two tubes closed at one end. Place a small piece of the mineral gypsum in the bottom of one of these tubes and heat. Drops of water will be seen to condense in the upper part of the tube.

Heat a weighed amount of gypsum in a porcelain crucible, and from the weight of the residue determine what per cent of water gypsum contains. Repeat the experiment with sal soda.

What are deliquescent compounds? Efflorescent compounds? Expose a piece of solid potassium hydroxide to the air. Do the same with some crystals of sodium sulphate.

What are oxides? Give examples.

What are hydroxides? Give examples.

What are acids? Give examples. (Study litmus.)

What are salts? Give examples.

NOTE.—The last four questions indicate a classification to which nearly all chemical compounds may be referred.

What is a primary salt? A secondary salt? A basic salt?
A double salt?

CHAPTER II.

NOMENCLATURE.

List of Acids and Formulas.

Hydrochloric acid	HCl ;	Chloric acid	HClO_3
Hydrobromic acid	HBr ;	Bromic acid	HBrO_3
Hydriodic acid	HI ;	Iodic acid	HIO_3
Hydrosulphuric acid	H_2S ;	Sulphuric acid	H_2SO_4
Hydroferrocyanic acid	$\text{H}_4\text{FeC}_6\text{N}_6$;		
Hydroferricyanic acid	$\text{H}_4\text{FeC}_6\text{N}_6$;		
Nitrous acid	HNO_2 ;	Nitric acid	HNO_3
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$;	Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$
Carbonic acid	H_2CO_3 ;	Phosphoric acid	H_3PO_4
Arsenious acid	H_3AsO_3 ;	Arsenic acid	H_3AsO_4
Tartaric acid	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$;		

NOTE. — Very much depends upon a thorough and familiar acquaintance with the foregoing list of acids and their formulas.

From the preceding list it will be noticed that acids may be divided into two classes, (1) those containing oxygen and (2) those which do not contain that element. The former are called *oxacids*, the latter *hydracids*. And again, of two oxacids differing in the amount of the oxygen, that one having the greater amount is given a name terminating in *ic*, the other in *ous*. Classify the above list.

That portion of the hydrogen of the acid which is capable of being displaced by a metal in the formation of a salt is spoken of as the *exchangeable hydrogen*, the remainder of the acid as the *acid radical*. Illustrate.

The exchangeable hydrogen may not be all of that element contained in the acid. For example, acetic acid contains four atoms of hydrogen, and only one of them capable of being displaced by the metal.

What are bi-basic and tri-basic acids? Find illustrations in the above list.

Nomenclature of Salts.

The laws governing the nomenclature of salts are very simple, and have universal application.

(1) If the salt has been formed from a hydracid, its name terminates in *ide*.

(2) An *ic oxacid* gives rise to salts which terminate in *ate*, and

(3) *ous oxacids* form salts in *ite*.

The laws which govern the naming of salts may be summarized as follows :

$$\text{ACIDS} \left\{ \begin{array}{l} \text{OXACIDS} \dots \left\{ \begin{array}{l} \text{ic form salts in } \textit{ate}. \\ \text{ous form salts in } \textit{ite}. \end{array} \right. \\ \text{HYDRACIDS} \dots \dots \text{form salts in } \textit{ide}. \end{array} \right.$$

Let the student illustrate the above laws by numerous examples.

Having the formula of an acid, how may you give its name?

What simple test is usually employed to determine whether a given substance is acid or not?

Neutralization.

Chemical substances are either *acid*, *alkaline*, or *neutral* to litmus paper.

Carefully neutralize a given measured quantity of dilute HCl with dilute NaOH and note the quantity of the alkali necessary for the purpose. Make another test with the same substances, using different quantities. If great care is taken,

and the exact point of neutralization ascertained each time, the four amounts used will approximately form a proportion.

Measure the amounts of solution used in each case by means of a burette, and ascertain whether acid, alkali, or neutral, with litmus paper.

Considering the last experiment, is neutralization a physical or a chemical action?

What is formed when HCl is treated with NaOH ?

Repeat the above experiment with KOH and HNO_3 ; with NH_4OH and $\text{HC}_2\text{H}_3\text{O}_2$; with NH_4OH and HCl ; with NaOH and HCl .

Exercises in Naming Salts from their Formulas.

Name the compound represented by the formula K_2SO_4 .

If you cannot readily do so, determine what it is by answering the following questions:

1. What metal does it contain?
2. What acid is represented in it?
3. Is this an oxacid or a hydracid?
4. If the former, is it ic or ous?
5. How does the salt name terminate which is formed from this acid?

Having answered these questions, we are ready to affirm that the given salt is Potassium Sulphate.

In like manner name the following:

CaSO_4 , $\text{Ca}(\text{NO}_3)_2$, KNO_3 , $\text{KC}_2\text{H}_3\text{O}_2$, NaCl , FeCl_2 , FeCl_3 ,
 SbCl_3 , (What is the valency of Sb ?), K_3PO_4 , $\text{Ca}_3(\text{PO}_4)_2$,
 AgCl , $\text{Pb}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$, NaNO_3 , CaHPO_4 , $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$,
 $\text{K}_3\text{FeC}_6\text{N}_6$, $\text{K}_4\text{FeC}_6\text{N}_6$, Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4 , $\text{K}_2\text{C}_2\text{O}_4$,
 $\text{Ca}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$ (Stearic acid), SeCl_4 , MgBr_2 .

Exercises in Writing Formulas.

Write the formula for Potassium Sulphate. In order to do this intelligently and with confidence, hold in mind the following points :

1. What acid is suggested by the name ?
2. What is the formula for this acid ?
3. What is the valency of the acid radical ?
4. What is the symbol and valency of the metal ?
5. The number of "bonds" of the metal must equal those of the acid radical in every satisfied compound.

The formula is therefore K_2SO_4 .

In a like manner write the formulas for the following :

Sodium	}	{	Chloride
Potassium			Acetate
Calcium			Sulphate
Lead			Sulphide
Iron			Nitrate
Silver			Oxalate
Bismuth			Phosphate
Magnesium			Ferrocyanide

The student may practice writing formulas for salts formed by each of the following metals with each of the following acids :

Sodium	}	{	Hydrochloric Acid
Magnesium			Carbonic Acid
Bismuth			Hydrosulphuric Acid
Calcium	}	{	Phosphoric Acid
Zinc			Acetic Acid
Copper			Sulphuric Acid
Cobalt			Nitric Acid

CHAPTER III.

THE LABORATORY.

Make a complete inventory of the chemicals on your table, classifying them into salts, bases, acids, etc.

Make an inventory of the apparatus, using the correct technical name for each article.

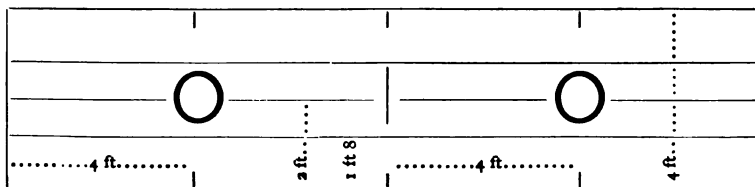
Do the same for the material to be found on the General Table.

What condition are these chemicals in when purchased for the laboratory?

How have they been prepared for use?

It is very desirable that each student should have a separate laboratory table, on which may be kept certain chemical reagents and apparatus for his personal use.

A convenient working laboratory for eight students may be easily arranged as follows: a strong, well built table, sixteen feet long and four feet wide, extends from one side into the middle of the room. Lengthwise, through the middle of the table, rises a partition, upon which are the shelves for holding the reagent bottles. One shelf, one foot above the surface of the table and four inches wide, is sufficient for each table. Two wash bowls situated as indicated in the diagram will serve for eight students.



A cask or tank in the attic or upper part of the room may be connected with the rain pipes on the roof, or filled from the public water supply, and thus made to supply water to the wash bowls, while other pipes conduct away the waste liquids.

In case illuminating gas can be had, each table should be supplied with a Bunsen burner. If gas can not be had, the alcohol lamp may be used, which will give good results.

Cupboards and drawers may be constructed underneath the table, which will be convenient for storing the student's laboratory apron or any larger pieces of apparatus.

The laboratory should be well ventilated, some arrangement being especially necessary for conveying away noxious gases.

Besides these work tables there should be a "general table," so situated as to be of easy access by all the students of the class.

The liquid reagents should be kept in glass stoppered bottles, and preferably with labels blown in the glass.

The names of sufficient reagents are given in the following table fully to identify and separate the twenty-five more commonly occurring metals, and the acids with which they are usually combined.

The names and formulas are given, with the number of parts by weight of water required to dissolve one part of the substance. The first nineteen mentioned may be kept on the student's table.

NOTE. — The *order of naming* the reagents in the following list will indicate a convenient arrangement for the laboratory tables.

NAMES.	FORMULAS.	PARTS OF H_2O .
Hydrochloric Acid,	HCl ,	24 per cent acid.
Nitric Acid,	HNO_3 ,	32 per cent acid.
Sulphuric Acid,	H_2SO_4 ,	Concentrated.
Acetic Acid,	$HC_2H_3O_2$,	30 per cent acid.
Hydrosulphuric Acid,	H_2S ,	Saturated solution.
Ammonium Hydroxide,	NH_4OH ,	10 per cent of gas.

NAMES.	FORMULAS.	PARTS OF H ₂ O.
Ammonium Chloride,	NH ₄ Cl,	1 : 8.
Carbonate,	(NH ₄) ₂ CO ₃ ,	1 : 4+1 part NH ₄ OH.
Sulphide,	(NH ₄) ₂ S,	NH ₄ OH Saturated with H ₂ S.
Oxalate,	(NH ₄) ₂ C ₂ O ₄ ,	1 : 24.
Potassium Dichromate,	K ₂ Cr ₂ O ₇ ,	1 : 10.
Sulphate,	K ₂ SO ₄ ,	1 : 12.
Ferricyanide,	K ₃ FeC ₆ N ₆ ,	1 : 12.
Hydroxide,	KOH,	1 : 8.
Calcium Sulphate,	CaSO ₄ ,	Saturated solution.
Chloride,	CaCl ₂ ,	1 : 8.
Barium Chloride,	BaCl ₂ ,	1 : 10.
Silver Nitrate,	AgNO ₃ ,	1 : 20.
Lead Acetate,	Pb(C ₂ H ₃ O ₂) ₂ ,	1 : 10.
Mercurous Nitrate,	Hg ₂ (NO ₃) ₂ ,	1 : 20+HNO ₃ .
Mercuric Chloride,	HgCl ₂ ,	1 : 16.
Arsenic Chloride,	AsCl ₃ ,	As ₂ O ₃ +HCl.
Antimony Chloride,	SbCl ₃ ,	1 : 10 Acidulated with HCl.
Stannous Chloride,	SnCl ₂ ,	1 : 10 Acidulated with HCl.
Bismuth Nitrate,	Bi(NO ₃) ₃ ,	H ₂ O+NH ₄ O ₃ .
Copper Sulphate,	CuSO ₄ ,	1 : 12.
Cadmium Chloride,	CdCl ₂ ,	1 : 12.
Ferrous Sulphate,	FeSO ₄ ,	1 : 10.
Ferric Chloride,	FeCl ₃ ,	1 : 10.
Aluminum Sulphate,	Al ₂ (SO ₄) ₃ ,	1 : 10.
Chromium Sulphate,	Cr ₂ (SO ₄) ₃ ,	1 : 10.
Cobalt Nitrate,	Co(NO ₃) ₂ ,	1 : 10.
Nickel Nitrate,	Ni(NO ₃) ₂ ,	1 : 10.
Manganese Chloride,	MnCl ₂ ,	1 : 10.
Zinc Sulphate,	ZnSO ₄ ,	1 : 10.
Barium Chloride,	BaCl ₂ ,	1 : 10.
Strontium Chloride,	SrCl ₂ ,	1 : 10.
Magnesium Sulphate,	MgSO ₄ ,	1 : 10.
Potassium Iodide,	KI,	1 : 20.
Potassium Sulphocyanide,	KCNS,	1 : 10.
Sodium Chloride,	NaCl,	1 : 10.
Sodium Hydrogen Phosphate,	Na ₂ HPO ₄ ,	1 : 10.
Potassium Ferrocyanide,	K ₄ FeC ₆ N ₆ ,	1 : 12.
Alcohol,	C ₂ H ₅ OH,	Proof Spirit.
Ammonium Molybdate,	(NH ₄) ₂ MoO ₄ ,	dissolve 1 part of Molybdic Acid in 4 parts of Ammonia, and pour the solution into 15 parts of dilute Nitric Acid of s.g. 1.20 (equal parts Nitric Acid and water). Let stand a day or two and filter.



Dry Reagents.

Sodium Carbonate,	Na_2CO_3 , or NaHCO_3 ,
Sodium Borate (Borax),	$\text{Na}_2\text{B}_4\text{O}_7$.
Potassium Chlorate,	KClO_3 .
Nitrate,	KNO_3 .
Ferrous Sulphide,	FeS .
Sulphate,	FeSO_4 .
Metallic Zinc,	Zn .
Microcosmic Salt,	$\text{HNaNH}_4\text{PO}_4$; made by dissolving 7 parts Na_2HPO_4 and 1 part NH_4Cl in 2 parts of boiling water and crystal- lizing.

NOTE. — Other salts of the above metals may be kept on hand to furnish a variety of material for the analysis of "unknowns." Obtain the large and instructive catalogues of dealers in chemicals and chemical apparatus.

Apparatus for Student's Table.

- Twelve test tubes, 4 inch.
- One test tube stand.
- Two test tubes, 8 inch and large diameter.
- Two beakers, 4 and 6 ounces.
- Two funnels, 3 and 4 inches in diameter.
- Two evaporating dishes, 3 and 4 ounces capacity.
- One platinum foil, one inch square.
- One platinum wire, 3 inches, mounted in handle of glass tubing.
- One pair forceps, of steel or nickel.
- One alcohol lamp, 4 ounces, or Bunsen burner.
- One wash bottle, 6 ounces capacity.
- One match safe.
- A blow pipe.
- One sand bath, a shallow sheet iron dish containing clean sand.
- One ring stand, for supporting funnels, evaporating dishes sand baths, generating flasks, etc.
- Litmus paper, cut into strips 1 inch long and 4-10 inches wide, and kept in a box or wide-mouthed bottle.
- One package filter paper, 4 inches in diameter.

One Marsh's apparatus, consisting of large test tube fitted with delivery tube.

One solid glass stirring rod, 6 inches in length and rounded at the ends.

One wash bowl.

A towel.

A common memorandum book.

A blank book for permanent notes, 3 or 4 quires.

The student should also provide himself with an apron made of strong material, and large enough to thoroughly protect his clothing from injury by acids and other chemicals.

A word may be said just here in regard to the cost of fitting up the laboratory described in this chapter.

A reliable firm, dealing in chemicals and supplies, estimates the cost as follows :

FOR STUDENT'S TABLE.

19 Reagents Bottles	\$2.85
Reagents for same	1.52
Apparatus	<u>5.55</u>
Total	\$9.92
Cost of student's tables for a class of eight, or sixteen if divided into two sections	79.36

FOR GENERAL TABLE.

Reagent Bottles	\$3.90
Reagents for same	12.60
Dry Reagents	<u>2.50</u>
Total cost for well equipped laboratory for any High School	\$98.36

To the Student.

The student must not suppose that his acquirements are to be confined to the facts and principles which he actually discovers in his laboratory work. This idea would defeat the very end had in view in establishing laboratory courses, that end being that he may be brought into living sympathy and



personal contact with the researches of the great men who have built up the body of chemical science, and made it what it now is. The laboratory work has not accomplished its purpose unless it has stimulated the desire to consult authorities for further information. Every laboratory, therefore, should have its working library, larger or smaller, of standard reference books.

A few volumes are here mentioned that will prove to be very helpful in this direction, if indeed they ought not to be considered as indispensable for successful work :—

Prescott and Johnson's Qualitative Analysis, latest revised edition.

Smith's Richter's Inorganic Chemistry.

Remsen's Chemistry, larger work.

Elliot and Storer's General Chemistry.

Shepard's Chemistry.

Roscoe and Schorlemmer's Treatise on Chemistry.

CHAPTER IV.

SOLIDS AND LIQUIDS.

To Change Solids into Liquids.

The analytical processes developed in this book are such as can only be carried on by first obtaining the substance to be examined in the liquid state. It therefore becomes necessary that we shall be able by one method or another to reduce all substances to a state of solution.

Of substances

- (1) Many readily dissolve in water,
- (2) Some not so readily,
- (3) Others not at all.

The first are spoken of as *soluble*, the second *sparingly soluble*, and the third *insoluble*.

1. Water used as a solvent forms a *physical solution*; that is to say, the substance after solution is chemically the same as when in the solid state, the chemical properties of the solid being retained while in the liquid state.

Solution:— Dissolve 2 grams of salt in 20 cc. of water; taste the solution; evaporate to dryness, and weigh the residue; taste the residue

Take a quantity of common salt; notice its crystalline structure; taste it; treat a small quantity in a test tube with water; treat a small quantity in a test tube with sulphuric acid, and notice the color and odor of the gas given off; moisten a glass rod with silver nitrate and hold it in the escaping gas.

We have now some acquaintance with common salt. It is a substance, (1) highly crystalline, (2) soluble in water, (3) has a peculiar taste, (4) with sulphuric acid yields a colorless gas of strong, irritating odor, which precipitates silver nitrate on a glass rod.

Now evaporate the water solution, and examine the substance recovered



by the operation. Is it common salt? These experiments have illustrated what is meant by a physical solution.

The varying solvent power of water toward different substances, as well as a proper conception of what is meant by a saturated solution, may be understood by the following experiments:

Take 10 cc. of distilled water in a test tube; add 1 gram of potassium carbonate; shake well, and if it dissolves add another gram of the salt; continue this until no more will dissolve.

In the same way determine the solubilities of potassium nitrate, potassium sulphate, calcium sulphate, sodium chloride.

2. A substance insoluble in water may be soluble in acids. In this case chemical action takes place, there is a loss of the original properties, and a *chemical solution* is the result.

Take a small piece of crystallized limestone, calc spar; taste it; boil it in water; treat a small piece in a test tube with hydrochloric acid, and notice odor and appearance of gas given off; pass the gas into lime water.

Calc spar can now be characterized as a substance, (1) crystalline, (2) tasteless, (3) insoluble in water, (4) soluble in hydrochloric acid, (5) with HCl yields a gas which renders the lime water turbid.

Now evaporate the solution obtained by the HCl, and ascertain whether the substance obtained is calc spar or not.

The experiment shows that when calc spar is dissolved in HCl it loses its character, and a substance has been formed with entirely different properties.

The acids most used as solvents in the chemical laboratory are HCl, HNO₃, and nitro-hydrochloric acid, or *aqua regia*. These are successively used in the order named, using in each case the acid diluted in water, but afterwards, if necessary, boiling the substance in the concentrated acid.

NOTES:—(a) Whether the solvent has effected a solution of any part of the substance may be ascertained by evaporating a drop or two of the liquid on platinum foil. If any has dissolved, a solid residue will be left on the foil.

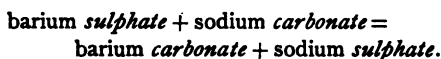
(b) The acid solutions should be evaporated nearly to dryness, and redissolved in water before proceeding with the analysis.

(c) Nitro-hydrochloric acid is made as it is needed by mixing three parts reagent HCl with one part of HNO₃. The reaction may be as follows, $3\text{HCl} + \text{HNO}_3 = \text{NOCl} + 2\text{Cl} + 2\text{H}_2\text{O}$. In this case the active agent in effecting the solution is the nascent chlorine.

3. A third condition of solubility is met with in those substances which can not be dissolved in water or acids. Such

may be fused on the platinum foil with potassium or sodium carbonate. This breaks up the given substance and recombines it in a form which is now soluble.

For example, if barium sulphate is fused with sodium carbonate an interchange will be effected producing barium carbonate and sodium sulphate,



The sodium sulphate is soluble in water, and the barium carbonate in dilute acid.

It will further be noticed that the *metal* of the given salt is to be found in the part which is insoluble in water, but soluble in acid, while the *acid radical* is found in the water solution.

4. Sometimes the alkali hydroxides are useful as solvents.

The alkali hydroxides generally form solutions which in character may be considered as lying between the merely physical and the true chemical solution; they may be called physico-chemical solutions. An example of this is seen in the solution of silver chloride in ammonium hydroxide, the resulting solution $(\text{NH}_4)_2(\text{AgCl})_2$ being a loose union of the two compounds. See page 38.

To Change Liquids into Solids.

It is sometimes desirable to convert substances which are in solution to the solid state.

This may be done by *evaporation* or *precipitation*.

In the former case the solution is slowly heated in an evaporating dish until the water is driven off and the solid substance obtained as a residue.

Evaporate 100 cc. of a solution of some salt; weigh the residue, and determine the proportion of the salt to the water in the solution.

Evaporate in a dish of known weight 70 cc. of well-water to dryness; weigh the residue, and calculate the per cent of impurities dissolved in the water.

The weight of the residue from 70 cc. of water stated in milligrams will be at the same time the number of grains per gallon. Why?

In the latter, a change is produced by which a new substance is formed insoluble in the menstruum present.



Add hydrochloric acid to silver nitrate; silver chloride is formed, insoluble in water, and hence it appears as a precipitate. In the same way bring solutions of barium chloride and potassium carbonate together and explain what happens.

As in dissolving by water, evaporation yields a substance of the same chemical composition as the solution; while by precipitation chemical action changes the composition and character of the substance.

CHAPTER V.

CHEMICAL EQUATIONS.

What is a chemical equation?

What does it teach?

Laboratory Work. — Mix the substances (in solution unless otherwise stated) together, as indicated by the first member of the equations under "Examples for Practice," p. 29. Observe carefully what takes place, and having learned, on good authority,* the composition and character (whether soluble or insoluble) of at least one of the resulting compounds, finish the equation.

Do not make the writing of equations simply an algebraic operation for this will often lead you into grave errors; but find some starting point either in observed phenomena or good authority.

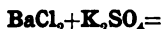
It would be well if some system of notation should be adopted by which precipitates, gaseous compounds, and solutions might be distinguished; e. g., precipitates may be underscored, gaseous compounds marked with a wavy line above the symbol, and solutions left without any accompanying mark.

Three Typical Cases are here discussed, in order to illustrate the method and spirit of this important part of the work of the student in chemistry.

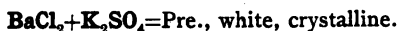
(1) For example, having mixed solutions of barium chloride and potassium sulphate together, it is required to write the equation.

* Prescott and Johnson's "Qualitative Chemical Analysis" may be consulted as authority on any or all of the reactions suggested in this book.

The first member contains the substances brought together thus :



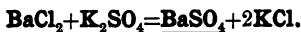
When the substances are mixed it is noticed that a dense white precipitate is formed, and the memorandum is made :



Reference to authority teaches that the precipitate is barium sulphate, BaSO_4 , and the equation stands :



Now consider (1) in forming BaSO_4 what elements have been liberated? and (2) will these unite with each other? Two atoms of Cl are set free from the BaCl_2 , and two atoms of K from the K_2SO_4 , just enough in the two cases to make two molecules of KCl. As potassium chloride is a well known compound, we conclude that the completed equation is :



What property of the barium sulphate caused it to be thrown down as a precipitate?

Why did not the potassium chloride precipitate?

Record the answers to the last two questions in the table of solubilities on page 31.

TO THE STUDENT : — It is of the utmost importance to your work that you early acquire the habit of reducing every case of chemical action which you study to the form of the equation. By doing so you are enabled to understand and appreciate many elements of the problem which otherwise would escape your notice.

Some of the points thus to be noticed are : the relative number of molecules of each substance taking part in the transaction ; the relative amounts by weight, and the relative affinities of atoms for each other. Again, by the equation may oftentimes be determined the true historical succession of events, what the initial movement was, what influence produced that movement, the next in order, and so on.

As a means of mental culture and discipline there is no more fruitful field than the writing, discussion, and interpretation of the chemical equation.

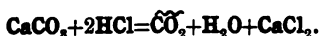
When was the chemical equation first used? Consult Roscoe and Schorlemmer's Treatise on Chemistry, vol. iii., pt. i., p. 7.

A Second Illustration. — Calcium carbonate, CaCO_3 , in the solid state is treated with hydrochloric acid.

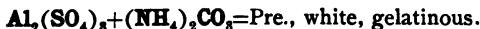
It is noticed that a gas is given off which, when tested (?), proves to be carbon dioxide, CO_2 . The equation will then read :



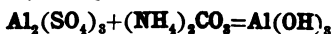
Now, the HCl must have been separated into its elements H and Cl. The CaCO_3 yields CO_2 , and the question arises as to the character of the compounds resulting from the recombination of these elements, Ca, O, H, and Cl; how will they unite? Ca and H will not unite with each other. Why? H and O have a strong affinity for each other, and calcium chloride is a well known compound. The conclusion is thus forced upon us that calcium chloride and water are the resulting compounds. Further, if water is formed there must have been two molecules of HCl decomposed for every one of the CaCO_3 . These two molecules of HCl will furnish the two atoms of H for a molecule of water, and at the same time two atoms of Cl for a molecule of calcium chloride. The equation will therefore stand :



A Third Illustration. — A solution of alum, $\text{Al}_2(\text{SO}_4)_3$, is treated with ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, and a white precipitate results. Thus :



Authority teaches that when these two compounds in solution are brought together there invariably results aluminum hydroxide, $\text{Al}(\text{OH})_3$,



First we notice that since the molecule of $\text{Al}_2(\text{SO}_4)_3$ contains two atoms of Al and each molecule of the $\text{Al}(\text{OH})_3$ contains but one atom of Al, there must have been two molecules of the precipitate formed.

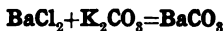
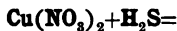
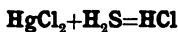
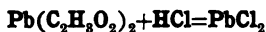
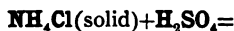
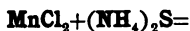
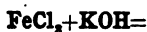
It is now evident that neither the element H nor the group OH is furnished by either of the compounds used, and that something else took part in the reaction. The only other substance present is water, and it must be that this has been decomposed. Moreover, there must have been six molecules decomposed to yield the six molecules of hydroxyl, OH, contained in the aluminum hydroxide. The equation will then take the form :



Again, the Al of the precipitate comes from the decomposition of one molecule of $\text{Al}_2(\text{SO}_4)_3$. This would set free three molecules of the sulphuric acid radical, SO_4 , which in turn unites with NH_4 to form $(\text{NH}_4)_2\text{SO}_4$, and since there are three molecules of SO_4 , there will be formed three molecules of $(\text{NH}_4)_2\text{SO}_4$, making it very certain that three molecules of the $(\text{NH}_4)_2\text{CO}_3$ were broken up. These latter molecules at the same time set free three molecules of CO_2 and three atoms of O. The three atoms of O unite with the six atoms of H from the water, and form three molecules of H_2O . The completed equation will therefore be :



Examples for Practice.





Practical Suggestions.

The most scrupulous neatness of work table and apparatus is necessary if correct results are to be attained in chemical analysis. Especial care must be taken not to contaminate the chemicals in the reagent bottles, either by laying down the stoppers while using, allowing the bottle to stand open, or by returning material after it has once been taken from the bottle.

Use small quantities, both of the substance to be analyzed and the reagent. Add reagents cautiously, drop by drop, in quantities sufficient for complete precipitation and separation.

When the work requires that the reagent shall be added "to alkaline or acid reaction," use the test paper to know when that point is reached.

Dilute solutions require more time for chemical action to take place. In all cases be deliberate; take time to observe all that occurs.

Heat facilitates chemical action in the majority of cases, although sometimes cold is necessary.

A most valuable as well as necessary feature of the student's work is the manner in which he keeps his notes. Scientific accuracy requires that the notes shall be taken as work proceeds, "while the test tube is still in his hand." They should record the conditions under which the test was made, all the phenomena of the reaction, and the conclusions to be drawn from them: (1) what has been done, (2) what has been observed, (3) what conclusions have been reached.

In which is to be recorded the solubility of all compounds as fast as they are observed.

Soluble in water, **S**; insoluble in water, **I**; insoluble in water, but soluble in acids, **S'**.

METALS.	Chloride	Sulphide	Sulphide+HCl	Carbonate	Hydroxide	Acetate	Nitrate	Bromide	Iodide	Sulphate	Chlorate	Chromate	Ferrocyanide	Ferricyanide	Phosphate	Oxalate
Ag																
Pb																
(Hg ₂)''																
As																
Sb																
Sn																
Hg''																
Bi																
Cd																
Cu																
Fe''																
Fe'''																
Cr																
Al																
Co																
Ni																
Mn																
Zn																
Ba																
Ca																
Sr																
Mg																
K																
Na																
NH ₄																
Li																

Columns may be added to this table for any other salts, the solubility of which it is desirable to record.

CHAPTER VI.

GROUPING OF THE METALS.*

As a step toward the discovery of schemes of analysis by which the metals most commonly occurring can be identified in unknown compounds, it is first desirable to divide them into a limited number of well defined groups, the members of which shall have some common chemical characteristics.

The commonly occurring metals are as follows : †

**Ag', As''', Fe'', Fe''', Ba'', K', Pb'', Sb''', Al''',
Ca'', Na', (Hg₂)'' (Mercurous), Hg'' (Mercuric), Cr''',
Sr'', (NH₄)', Mn'', Mg'', Sn'', Sn^{iv}, Cu'', Bi''',
Cd'', Zn'', Co'', Ni''.**

A common reagent, HCl, is chosen and its behavior with a single salt of each of the above metals carefully studied. ‡

The problem before the student, therefore, is to answer the question :

1. How are salts of the above metals affected by treating them with reagent HCl?

The answer to this question can only be found by making the necessary tests in the laboratory.

* By the heading of this chapter it is not to be understood that the qualitative chemist investigates the metals themselves. In the great majority of cases of chemical action it is some compound of the metal, and not the metal in the elemental state that is involved. The whole subject of the grouping of the metals and the subsequent chapters on the separation of the metals may be traversed, and the student never see the metals as such. Indeed, it may be that he will never see some of the metals which play the most common and important part in applied chemistry. By their very nature, such metals as calcium and barium, potassium and sodium, never can be practically used.

† The valency of the metals as indicated in the above list should be fixed in mind.

‡ The work in this chapter is divided into eight lessons, indicated by the wider spacings. Thus, the first lesson would be simply question (1), and might require two days of laboratory and class room work; the second lesson would be questions (2) to (8) inclusive; question (9) would constitute another long lesson; question (10) to (16) inclusive another, and so on.

About five cubic centimeters of the solution to be tested are taken in a test tube, a few drops of the reagent added, and the result, precipitate or no precipitate, noted.

The student's work and note book will proceed as follows :

$\text{AgNO}_3 + \text{HCl} = \text{Pre.}$, white, heavy.

$\text{AgNO}_3 + \text{HCl} = \underline{\text{AgCl}} + \text{HNO}_3$.

$\text{AsCl}_3 + \text{HCl} = \text{No Pre.}$ (Could there be any action here ?)

$\text{FeSO}_4 + \text{HCl} = \text{No Pre.}$

$\text{Fe}_2(\text{SO}_4)_3 + \text{HCl} = \text{No Pre.}$

BaCl_2 may be found in solution on the general table. From this fact, taken with another, viz., that if a reaction occurred between any **Ba** salt and HCl , BaCl_2 would result, we conclude that no salt of **Ba** will precipitate with HCl .

$\text{K}_2\text{SO}_4 + \text{HCl} = \text{No Pre.}$

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{HCl} = \text{Pre.}$, white, heavy, crystalline.

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{HCl} = \underline{\text{PbCl}_2} + 2\text{HC}_2\text{H}_3\text{O}_2$.

SbCl_3 may be found in solution, and hence (see **Ba** above) no **Sb** salt will precipitate with HCl .

The work should be thus carried on until at least one salt for every metal is tested. When this is done a proper response to question (1) can be given.

2. What division into *two groups* is suggested by (1) ?
3. What chlorides are insoluble in water ?
4. What constituent element of the HCl enters into these precipitates ?
5. What class of salts contains this element ?
6. How would any such salts affect salts of **Pb**, **Ag**, and $(\text{Hg}_2)''$? What broad generalization is here reached ?
7. What constituent element of the salt enters into these precipitates ?
8. Would any salt of **Pb**, **Ag**, and $(\text{Hg}_2)''$, in solution, be precipitated by HCl ? By any chloride ? What broader generalization is here reached ?

A new reagent, hydrosulphuric acid, H_2S , is now taken, and answers found to a question similar to (1), viz. :

9. How do the given salts behave when treated with H_2S ?

NOTE. — The reagent H_2S is made as it is wanted by passing the gas H_2S , generated from FeS and H_2SO_4 , into water until the solution smells strongly of the gas. Equation.

The answers to question (9) obtained by the different members of the class will vary somewhat, from the fact that, in the case of some of the metals, H_2S causes a precipitate to form very slowly, and with others producing simply a change of color. All the doubtful cases will be removed if a small amount of HCl be used with the H_2S as reagent. Let the student notice how promptly the lemon yellow arsenious sulphide forms when the solution is first acidulated with HCl . This raises a new inquiry, viz. :

10. How would the given salts be affected by H_2S in a solution to which HCl has been added?

The work done on (9) and (10) has illustrated the difference that may exist between the reagents chosen for a given work, as well as the principle on which such reagents are chosen. Hydrogen sulphide will not effect a sharp separation of metals into groups, because of its indifferent action on the salts of certain metals, but when combined with HCl the separation becomes clear and definite; there are no doubtful cases.

11. Considering questions (2), (9), and (10), what division into *three groups* is suggested?

12. What sulphides are insoluble in H_2O ? The work on question (9) has answered this.

13. What sulphides are insoluble in H_2O and HCl ? The work on (10) has answered this.

14. What constituent element of the H_2S enters into these precipitates?

15. What class of salts contains this element?

16. How would any of this class of salts change salts of Fe , Mn , Cu , Pb , Cd , Ca , or Mg ?

17. How would the given salts behave when treated with ammonium sulphide, $(\text{NH}_4)_2\text{S}$?

18. How do the given salts behave in the presence of ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$?

19. Would any other carbonate do for this test?

Suppose it were required to make barium carbonate, how could it be done? One answer to this question would be to combine barium chloride and ammonium carbonate. A broader answer would be, combine barium chloride with any soluble carbonate. Would that be true? A still broader answer would be, combine any soluble salt of barium with any soluble carbonate. Would that be true? Could any barium salt be combined with any carbonate to make barium carbonate?

20. Considering all you have learned, how may Ba, Ca, and Sr be separated from all the others?

21. What carbonates are soluble in water?

22. What carbonates are insoluble in water?

23. How are Mg salts affected by $(\text{NH}_4)_2\text{CO}_3$? Warm the solution a little if necessary.

24. How are Mg salts affected by NH_4Cl and $(\text{NH}_4)_2\text{CO}_3$? How by $(\text{NH}_4)_2\text{CO}_3$ and NH_4Cl ? What facts regarding the solubility of Mg salts have been learned?

25. How are Mg salts affected by $\text{NH}_4\text{Cl} + (\text{NH}_4)_2\text{CO}_3$ and Na_2HPO_4 ?

26. What metals may constitute a First Group? A Second Group? A Third Group? A Fourth Group? Mg may be considered as a member of the Fourth Group, but requiring a reagent, Na_2HPO_4 , peculiar to itself.

27. What metals are left to constitute a Fifth Group?

28. The most noticeable characteristic of the salts of the metals of the Fifth Group is their failure to precipitate when treated with any common reagent. Why?

REVIEW.

What chlorides are insoluble in water ?

What chlorides are soluble in water ?

What sulphides are insoluble in water ?

What sulphides are insoluble in HCl ?

What sulphides are soluble in HCl ?

What carbonates are insoluble in water ?

What carbonates are soluble in water ?

What are the metals of the First Group ? Second Group ? Third ? Fourth ? Fifth ?

What are the group precipitates of First Group ? Second Group ? Third ? Fourth ? Fifth ?

Classify and tabulate these group precipitates as to color, and also as to the valency of the metals contained in them.

The above questions should suggest many others that may be raised by student and teacher, in order *thoroughly to review* the work thus far gone over.

NOTE. — A scientific demonstration does not consist in simply making a single experiment and basing a conclusion upon it. On the contrary, no true scientist will announce a conclusion until he has tested it by many and repeated trials. Now, the work done in the laboratory by a large class makes such scientific demonstrations possible, and that without the expenditure of a large amount of time. If a class of twenty or thirty students, doing their work independently of each other, are agreed in regard to the outcome of an experiment, or series of experiments, the fact thus ascertained may be relied upon. A doubt expressed by one or more of the class calls for a review of their work, and perhaps of the work of the whole class.

TABLE OF GROUPING OF METALS.
Make up this table from the answers to the questions on the preceding pages.

PRECIPITATED BY	METALS WHOSE SALTS ARE PRECIPITATED.
Chlorides or HCl	
H₂S in acid solution	
Sulphides or H₂S	
Carbonates with NH₄Cl	
Carbonates	

CHAPTER VII.

SEPARATION OF METALS OF THE FIRST GROUP.

The most difficult metals to identify and separate are those of the second group, and hence it is desirable that this work shall be undertaken only after considerable experience in the handling of reagents and apparatus. It is therefore suggested that instead of following the order as indicated in the next few pages, the student study the separation of the metals of the first group, then pass to the fourth group, and from that to the fifth, the third, the second division of the second group, and, last of all, the separation of the elements As, Sb, and Sn.

It should be remembered, however, that in the systematic analysis of unknown compounds the order which has been developed in the grouping of the metals must be strictly adhered to; that is, the order of approach must always be first group, second, third, fourth, and lastly the fifth group. Why?

1. What are the metals of the first group?
2. In accordance with what fact already observed may they be separated from all other metals?
3. What then is the *group reagent*?
4. What are the *group precipitates*?

Before 5 and 6 are answered the group precipitates should be filtered and thoroughly washed with pure distilled water. The hot H_2O and NH_4OH may be added to the precipitate on the filter.

5. How are these affected by much hot water?
6. How by NH_4OH ? See under 4, page 24.
7. What is the composition of the solution which is obtained by the hot H_2O ?
8. Of the remaining chlorides, which one is soluble in NH_4OH ?

9. Does the NH_4OH produce any change in Hg_2Cl_2 ?
10. From 5 and 6 find a direct method of separating the metals in this group.
11. If only one metal is present in the first group precipitate, NH_4OH will determine which it is. How?

Confirmatory Tests.

The characteristic behavior above described of these first-group metals is usually sufficient for their determination; but, in cases of doubt, and especially in the examination of mixtures, other tests may be made which shall be confirmatory of the original analysis. The following will be found of value for this purpose:

For Lead. — Solutions of lead salts are precipitated by H_2SO_4 , sulphates, H_2S , sulphides, iodides, chromates, bromides, alkalis, carbonates, phosphates, oxalates.

The student should not fail to challenge each of the above statements with appropriate tests, recording the results, such as color and general appearance of precipitates, in his permanent note-book.

For Silver. — Solutions of silver salts are precipitated by the fixed alkalies (soluble in HNO_3 and $\text{HC}_2\text{H}_3\text{O}_2$); by the volatile alkali hydroxide (soluble in excess of reagent); by hydrosulphuric acid, alkali sulphides (soluble in HNO_3), bromides, iodides (soluble in excess), ferrocyanides, ferricyanides, carbonates, oxalates, and phosphates.

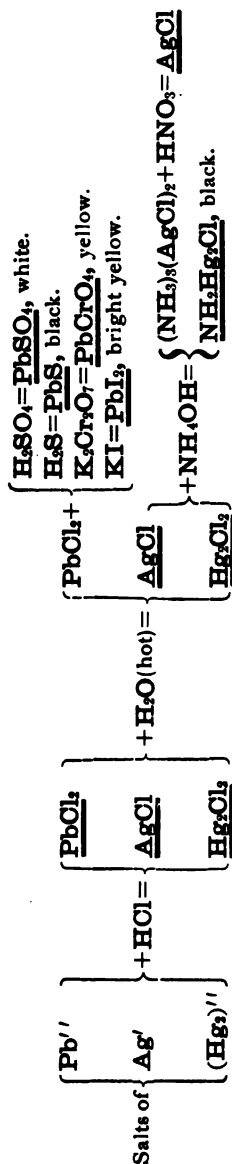
For Mercury in Mercurous Solutions. — The commonly occurring mercurous compounds are all insoluble in water, with the exception of the normal nitrate, and hence will be precipitated by the common reagents.

Alkali sulphides or hydrosulphuric acid precipitate, not mercurous sulphide, Hg_2S , but $\text{HgS} + \text{Hg}$, not soluble in HNO_3 . (Does this last distinguish Ag from Hg?)

12. May precipitations occur with HCl when no first group metal is present? Yes; consult Prescott and Johnson's "Qualitative Chemical Analysis," fourth revised edition, article 547.

SYNOPTICAL VIEW OF THE SEPARATION OF THE METALS OF THE FIRST GROUP.

A general view of the separation in Group I., in the form of a synopsis, is here given, that it may serve as a model for similar schemes which the student will be expected to make for himself for the succeeding groups.



It is understood in the above and similar synopses, which will subsequently be required to be made, that only the compound containing the metal in question in any reaction is given; and that, in order to make the presentation graphic, so that it will appeal to the eye, and impress itself on the memory, all precipitates are underscored, gaseous compounds are indicated by a wavy line above them, and symbols with no accompanying marks indicate substances in solution.

CHAPTER VIII.

OCCURRENCE IN NATURE AND USES OF METALS OF THE FIRST GROUP.

In what form is Ag found in nature?

Describe one process of separating Ag from its ores.

What salt of Ag is in most common use? What is it used for?

Fuse a piece of AgNO_3 with the blow pipe on charcoal.

What is an alloy? An amalgam?

What other metal besides Ag in our silver coins? Proportions of the two metals?

Are English coins more nearly pure than ours?

What is the chemistry of the photographic process? Ask the photographer.

Why do silver coins blacken when carried in the pocket with matches?

Why does a silver spoon blacken which has been used in beating eggs? Try the experiment.

What is the effect of using silver drinking cups with sulphur waters?

Potassium cyanide is a good solvent for silver sulphide, and is sometimes used for cleansing tarnished silver. It is poisonous, and should be used with caution.

In what form is Pb found in nature?

How is it separated from its ores? Fuse a lead salt on charcoal.

Some of its physical properties?

What is the effect of leaden water pipes on drinking water?

What is litharge? White lead? White paint?

What is the "lead" of lead pencils?

In what form is Hg found in nature?

How is Hg separated from its ores? Heat red oxide of mercury in a closed tube of hard glass.

What is corrosive sublimate? Calomel? Lunar caustic? Sugar of lead?

To a solution of AgNO_3 , containing about 5 grams of the salt in 100 cc of water, add a few drops of mercury, and allow it to remain for several days. The silver will separate in delicate crystals.

When does mercury become solid?

What is the specific gravity of Hg? of Pb?

Drop a small ball of iron or stone, a marble or a lead bullet, into mercury contained in a dish.

Drop a copper coin into a solution of corrosive sublimate. Explain.

Try HCl , H_2SO_4 and HNO_3 and find the true solvent for Hg.

CHAPTER IX.

SEPARATION OF METALS OF SECOND GROUP.

1. What metals constitute Group II. ?
2. Pb must be included in this group, as it is not completely separated as a chloride in the first group. Why?
3. After the metals of the first group have been set aside, what reagents will precipitate those of the second group and no others ?
4. What are the precipitates thus formed ?
5. How are these precipitates (filtered and washed) affected by yellow ammonium sulphide, $(\text{NH}_4)_2\text{S}_2$?

NOTE. — Ordinary colorless ammonium sulphide, $(\text{NH}_4)_2\text{S}$, which has stood for several weeks in the laboratory will be found to have acquired a yellow color, and its composition has changed to $(\text{NH}_4)_2\text{S}_2$.

6. What is the effect of applying HCl to the filtrate from (5) (a) if something has dissolved and (b) if nothing has dissolved ? (Try the effect of adding HCl to the $(\text{NH}_4)_2\text{S}_2$ by itself.)
7. Of the group precipitates insoluble in $(\text{NH}_4)_2\text{S}_2$, which are soluble in hot, moderately dilute HNO_3 ?
8. Of the nitrates thus formed, which are precipitated by H_2SO_4 ?
9. How do the remaining nitrates behave in the presence of NH_4OH added to alkaline reaction ?

Synopsis the work in this group as far as you have gone.

Separation of As, Sb, and Sn.

The method may be summarized as follows :

10. The sulphides which dissolved by $(\text{NH}_4)_2\text{S}_2$, (5), may be recovered by slightly acidulating with HCl which has first been

diluted with H_2S . Why? The As is thrown down as As_2S_3 , yellow, the Sb as Sb_2S_3 , orange, and the Sn as SnS_2 , yellow.

11. The precipitates are filtered and washed.

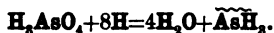
12. A minute particle of KClO_3 is immersed in the precipitate on the filter, and treated with a few drops of hot HCl . The As_2S_3 is dissolved as H_3AsO_4 , the Sb_2S_3 as SbCl_5 , the SnS_2 as SnCl_4 .



13. The excess of Cl is driven off (why?) by evaporation and the solution used in making Marsh's test.

Marsh's Test.

Generate H, using Zn and diluted H_2SO_4 , in a large size test tube provided with a suitable delivery tube, and when the gas is freely given off add the solution to be tested. Compounds of As and Sb in solution will be reduced by the H forming the gases AsH_3 and SbH_3 .



The gas thus formed is introduced into a solution of silver nitrate. It should not be allowed to escape into the air in any quantity as it is extremely poisonous.

A colored precipitate in the AgNO_3 solution indicates the presence of either As or Sb. If the former, it will be found in the filtrate, as H_3AsO_4 , after the excess of AgNO_3 has been precipitated by HCl and filtered out.* A yellow precipitate by H_2S in this solution is evidence of As.

The Sb enters into the precipitate as Ag_3Sb . After digesting this precipitate with hot HCl (why?), the filtrate will give an orange precipitate with H_2S , evidence of Sb.

If Sn is present, it will be left in the Marsh's generator as metallic tin, and may be identified by filtering, dissolving in

* AgCl is sparingly soluble in strong HCl , and hence the acid used should be dilute.

hot and dilute HCl and testing the solution, SnCl_2 , with HgCl_2 . A white precipitate of mercurous chloride, Hg_2Cl_2 , or a gray precipitate of metallic mercury, Hg, is evidence of Sn.

"Spot Tests" for As and Sb.

After adding the solution of arsenious acid or antimonious chloride to the Marsh's generator, and after the air has been completely expelled from the apparatus, the gas may be lighted and the flame held in contact with a cold, dry porcelain surface. Metallic As or Sb, as the case may be, is separated and deposited on the porcelain.

The deportment of these spots with certain reagents is strikingly different, so that these tests become important factors in the detection and separation of these elements. Let the student ascertain the change produced by the treatment of the spots by the following reagents :

- (a) A drop of hot HNO_3 .
- (b) A drop of concentrated alkaline solution of sodium hypochlorite.
- (c) Warmed with a drop of yellow ammonium sulphide.
- (d) Applying $(\text{NH}_4)_2\text{CO}_3$ to (c).
- (e) Adding HCl to (c).
- (f) Compare color, lustre, etc., of spots.*

Specimen Pages from Student's Note-Book.

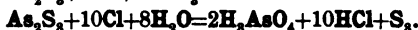
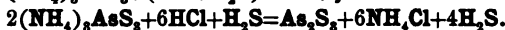
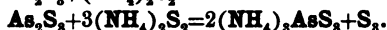
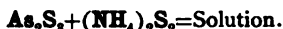
The following memoranda and equations will illustrate the condition of the student's note-book after his work on these metals in the laboratory is completed.

Arsenic.

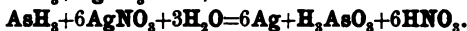
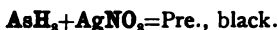


* See Prescott and Johnson's "Qualitative Chemical Analysis" for proper authority on the work. It should be insisted, however, that the class make the above experiments with known substances and compare results before looking into any authority.

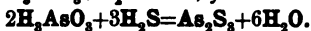
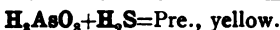
The precipitate is filtered, washed, and treated on the filter with yellow ammonium sulphide.



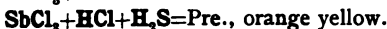
(Represent the last reaction by two equations showing the successive steps.)



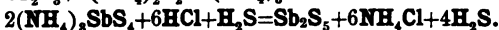
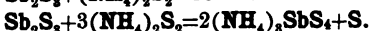
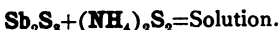
The excess of AgNO_3 is removed by HCl ($\text{AgNO}_3 + \text{HCl} = \underline{\text{AgCl}} + \text{HNO}_3$), and the filtrate is treated with H_2S .



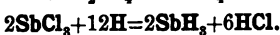
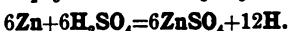
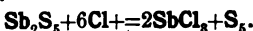
Antimony.



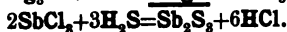
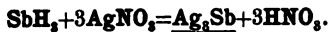
Precipitate filtered and washed.



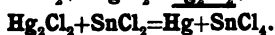
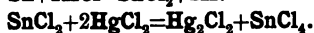
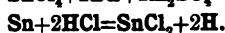
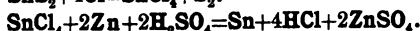
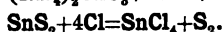
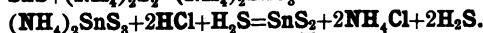
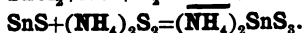
Precipitate filtered, washed, and treated on the filter with KClO_3 and HCl .



The last two equations show the reaction in Marsh's generator. (What is the nature of the work to be done in changing SbCl_3 into SbH_3 ? What chemical agent is fitted to do that work? How much H is needed to remove six atoms of Cl ? How much H_2SO_4 must be decomposed to furnish this? etc., etc.)



Tin.



Confirmatory Tests.

For Cadmium. — Solutions of Cd salts are precipitated by NaOH, NH_4OH (soluble in excess), $(\text{NH}_4)_2\text{S}$, KCN (soluble in excess), phosphates (soluble in acids), oxalates, ferrocyanides (soluble in HCl and NH_4OH), ferricyanides (with same solubilities as ferrocyanides).

For Copper. — A clean iron nail or knife blade immersed for a few minutes in a solution of copper salts acidulated with HCl separates metallic Cu. Equation?

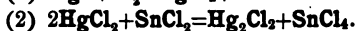
NaOH or KOH added to copper salts precipitate blue $\text{Cu}(\text{OH})_2$ which, on boiling, changes to black $\text{Cu}_2\text{O}_2(\text{OH})_2$; NH_4OH first forms a greenish, then a bluish precipitate which dissolves in excess to a deep blue solution, a very delicate test, yielding results in solutions containing one part of Cu to one hundred thousand parts of water.

Copper salts are precipitated by $(\text{NH}_4)_2\text{CO}_3$ (soluble in excess), K_2CO_3 , sulphides (soluble in HNO_3), phosphates, oxalates, chromates, alkali cyanides (soluble in excess), ferrocyanides, ferricyanides, iodides.

Mixtures of Cd and Cu salts may be separated by first precipitating both as sulphides, and then dissolving CuS by KCN; or hot dilute H_2SO_4 dissolves CdS and leaves CuS undissolved.

For Bismuth.— Study the action of the following reagents on a known solution of a bismuth salt and record the results for future use as confirmatory tests: water (in acidulated solutions), alkalies, carbonates, H_2S and sulphides, chromates, phosphates, oxalates, KI, KBr, KCN, ferrocyanides, ferricyanides.

For Mercury in Mercuric Compounds.— The black precipitate of HgS , insoluble in HNO_3 , is dissolved by nitro-hydrochloric acid and the solution treated with stannous chloride, SnCl_2 . A white precipitate is Hg_2Cl_2 ; the gray precipitate which finally appears is metallic mercury, Hg .



A bright strip of copper immersed in a solution of mercuric salt will be covered with metallic mercury. Another characteristic test for mercuric salts is the production of the yellowish red mercuric iodide, HgI_2 , soluble by excess to a double iodide, $\text{HgI}_2(\text{KI})_2$.

Synoptical View of Separation of the Metals of Second Group.

From the work on pages 43 to 47 make a synopsis of the work of separation in this group. See p. 40, and note on p. 56.

CHAPTER X.

OCCURRENCE AND USES OF SECOND GROUP METALS.

In what form is As found in nature? How separated from its ores?

Heat small pieces of the mineral realgar or orpiment in the bottom of a closed glass tube. If it is not too strongly heated, metallic arsenic will be left in the bottom of the tube and the sulphides of arsenic will sublime on the sides.

In another tube put a minute piece of arsenic trioxide, and just above it a small piece of charcoal. Heat gently. Explain the reaction.

What is the "arsenic" of the drug store?

Study the properties and uses of As.

What is Paris Green?

Especially, study the uses of As as a pigment in wall paper, children's hose, etc.

Composition and uses of Fowler's solution?

The antidote for arsenical poisoning is freshly precipitated ferric hydroxide, $\text{Fe}(\text{OH})_3$. It forms an insoluble compound with the arsenic in the stomach. Prove that this is true by the following experiment:—

Treat a dilute solution of H_3AsO_3 with freshly precipitated $\text{Fe}(\text{OH})_3$ (in excess), filter and test the filtrate for As.

How does Sb occur in nature? How separated?

What is tartar emetic? Cream of tartar? Butter of antimony?

In what form is Sn found? How is it prepared for commerce?

Its properties and uses? What is block tin? Tin plate? Pewter? Solder? Britannia? German silver?

Occurrence of Bi? Its chief uses? What are fusible metals?

Occurrence of Cu? Its properties and uses?

Separate the Ag of a ten cent piece from the Cu?

Describe the process of electroplating; of electrotyping.

What is brass? Bronze? Bell metal?

Occurrence of Cd? Its properties and uses?

NOTE. — Many of the rare metals, such as gold, platinum, palladium, iridium, and tellurium, are found in this group. Their sulphides are insoluble in water and dilute acids.

Gold which occurs mostly in the native state may be dissolved by nitro-hydrochloric acid to auric chloride, AuCl_3 . If, now, ferrous sulphate be added to this solution, metallic gold will be separated in a finely divided state. This may be fused to a yellow bead on charcoal.



For other tests, for this and the other noble metals, consult the larger works on qualitative chemistry.

CHAPTER XI.

SEPARATION OF METALS OF THE THIRD GROUP.

Make experiments as suggested in the table below, recording the results in the appropriate places as Pre. (precipitate) or No Pre. (no precipitate), marking any precipitates which dissolve in excess of reagents by a star, thus, Pre.*

REAGENTS ADDED	TO SOLUBLE SALTS OF											
	Fe''	Fe'''	Cr	Al	Co	Ni	Mn	Zn	Ba	Ca	Sr	Mg
KOH or NaOH, in excess												
NH ₄ OH, in excess												
NH ₄ Cl + NH ₄ OH, (both in excess)												
(NH ₄) ₂ CO ₃												
(NH ₄) ₂ S												
HCl + H ₂ S												

Questions on the Table Work.

What reagent precipitates all the metals of the third group and not those of the fourth?

How are these metals separated from those of the second group?

In mixtures of second and third group salts, the latter will be found in the filtrate from the second group precipitate and hence necessarily acid.

This being so, it is proper to consider (1) what effect this acid will have on the proposed group reagent, and (2) how this may be counteracted. The choice of NH_4OH for the latter purpose will necessitate further inquiries, viz.,

Will NH_4OH precipitate any of the metals of this group?

Will NH_4OH precipitate any salt beyond this group?

How may this be prevented?

What metals of this group are precipitated by NH_4Cl and NH_4OH ?

The above work has led to the division of the group into *two sub-groups*, the first containing the triad elements, Fe, Cr, Al, and the second those having a valence of two; but the method has this imperfection, that iron salts in the ferrous condition do not precipitate readily with NH_4Cl and NH_4OH , ferrous hydroxide being somewhat soluble in NH_4Cl . In order, therefore, that both forms of iron, ferrous and ferric, shall precipitate together, the former is oxidized to the ferric condition before applying the reagents NH_4Cl and NH_4OH .

These facts make it necessary that we should turn aside and make

A Study in Oxidation.

It is first necessary to be able to distinguish readily between ferrous and ferric compounds. The following table gives two characteristic tests for this purpose.

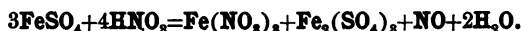
REAGENTS ADDED	TO SOLUTIONS.	
	Ferric	Ferrous
KCNS	Blood red solution.	No change.
$\text{K}_2\text{FeC}_6\text{N}_6$	Green solution.	Blue precipitate.

Let the student write the equations for these tests.

Oxidation.

The Method.—Take two cubic centimeters of a solution of a ferrous salt (identified to be such by the proper tests) in a test tube and add two or three drops of nitric acid. Boil for a minute or two or until the brown fumes pass away. The solution should now give the test for the ferric condition. By several tests determine the least amount of nitric acid necessary to accomplish the oxidation.

NOTE.—A reaction very similar to this occurs in the "brown ring test" for nitric acid, and its thorough study may be reserved until that point is reached. The equation for the oxidation is as follows:



In this connection several points should be noticed:

1. The value of HNO_3 as an oxidizing agent due to its unstable character (?) and its large proportion of oxygen.
2. The effect which the mere presence of an oxidizable substance, such as FeSO_4 , produces on the HNO_3 .
3. The evolution of the brown vapors, which is always the sign or indication that an oxidizing agent and an oxidizable substance have been brought together.
4. Iron in the filtrate from second group is necessarily ferrous, as hydrosulphuric acid, H_2S , acts on ferric salts as a *reducing agent*.



Make several tests to prove this.

Tests for Fe, Cr, and Al.—The salts in solution have been treated with HNO_3 , NH_4Cl , NH_4OH ; the hydroxides, $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, and $\text{Al}(\text{OH})_3$ have been precipitated; the precipitates have been filtered and washed.

Now pierce the point of the filter with a glass rod, and, with a small quantity of pure water, wash the precipitate into a test tube. Divide this precipitate into three portions.

For Iron.—Dissolve one portion in HCl and ascertain (a) how the solution is changed by KCNS , and (b) how the resultant solution is changed by HgCl_2 .

For Chromium.—Fuse a second portion of the hydroxide, supposed to be $\text{Cr}(\text{OH})_3$, on the platinum foil with an equal portion each of dry Na_2CO_3 and KNO_3 . A *yellow mass* indicates Cr.



Dissolve this yellow mass in H_2O , acidify with $\text{H}_2\text{C}_2\text{O}_4$, and add $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$; a dense yellow precipitate is a further indication of Cr.

For Aluminium.—Dissolve the third portion, supposed to be $\text{Al}(\text{OH})_3$, in KOH and add NH_4Cl in excess, or, slightly acidulate with HCl and add excess of $(\text{NH}_4)_2\text{CO}_3$. A precipitate in either case is $\text{Al}(\text{OH})_3$.

Tests for Mn, Zn, Co, Ni.—In case HNO_3 , NH_4Cl and NH_4OH have been applied to salts of metals of this group and no precipitate has resulted, what is the effect of adding $(\text{NH}_4)_2\text{S}$?

Of the sulphides thus produced, which are soluble in HCl ?

How do the chlorides thus formed behave in the presence of an excess of KOH ?

How is the Zn solution affected by adding $(\text{NH}_4)_2\text{S}$?

Fuse the insoluble $\text{Mn}(\text{OH})_2$ on the platinum foil with KNO_3 and Na_2CO_3 and note the *bright green mass*.



Make a transparent bead on the platinum wire with borax and moisten with the sulphides of Co and Ni. On further heating, characteristic *colors* will be developed, *blue* for Co and *brown* for Ni.

Confirmatory Tests.

For Ferrous Salts.—Solutions of ferrous salts are precipitated by KCN , reddish brown; $\text{K}_3\text{FeC}_6\text{N}_6$, dark blue, (how does this precipitate behave when treated with NaOH ?); $\text{K}_4\text{FeC}_6\text{N}_6$, bluish white; $(\text{NH}_4)_2\text{CO}_3$, white at first, but soon changing to reddish brown; Na_2HPO_4 , white to bluish-white. KCNS produces no change in ferrous salts free from ferric.

For Ferric Salts.—Solutions are precipitated by alkali hydroxides; alkali carbonates; ammonium sulphide; ferrocyanides (Prussian blue). Disodium hydrogen phosphate, Na_2HPO_4 , forms a yellowish white precipitate, if no free acid is present, easily soluble in mineral acids, insoluble in acetic acid.

Characteristic *colored solutions* are formed by sulphocyanides, blood red; ferricyanides, green or brown; acetates, dull red; sulphites, red.

Reducing agents change ferric into ferrous salts; test with HCl and Zn ; with H_2S ; with KI . Make the green solution by treating FeCl_3 with $\text{K}_3\text{FeC}_6\text{N}_6$ and then add a reducing agent, such as H_2S (?).

For Chromium.—Chromic hydroxide, $\text{Cr}(\text{OH})_3$, is precipitated from chromic salts by NH_4OH , KOH , $(\text{NH}_4)_2\text{S}$, and alkali carbonates.

For Aluminum.—Aluminum hydroxide, $\text{Al}(\text{OH})_3$, is precipitated from solutions of salts by $(\text{NH}_4)_2\text{S}$, NH_4OH , KOH (soluble in excess and reprecipitated by NH_4Cl), and by alkali carbonates. Of a grayish white color, gelatinous, floating in every part of the menstruum in which it forms, this precipitate is easily recognized and readily distinguished from all others.

For Manganese.—Manganese forms two classes of salts, manganous and manganic, the latter being somewhat unstable. Manganous salts are precipitated by alkali hydroxides, white, turning to brown in the air; $(\text{NH}_4)_2\text{S}$, flesh color; alkali carbonates, white to brown, and Na_2HPO_4 , white.

For Zinc.—Of zinc salts, the acetate, bromide, chloride, chlorate, chromate, iodide, nitrate, and sulphate are soluble in water; those insoluble in water are soluble in acids. The soluble salts have an acid reaction, metallic taste, and are poisonous.

Zinc salts are precipitated by all alkali hydroxides, white (soluble in excess); by $(\text{NH}_4)_2\text{S}$; by alkali carbonates, white; KCN , ferrocyanides, white; ferricyanides, yellowish.

SALTS OF	
NICKEL,	COBALT,
In crystalline condition and in solution,	
<i>green,</i>	<i>red,</i>
these dehydrated,	
<i>yellow,</i>	<i>blue.</i>
Treated with fixed alkali hydroxides,	
<i>green precipitate,</i>	<i>blue precipitate ;</i>
the hydroxide heated,	
<i>green precipitate,</i>	<i>red precipitate and finally brown.</i>
Treated with ammonium hydroxide,	
<i>greenish precipitate,</i>	<i>blue precipitate.</i>
Treated with ammonium hydroxide in excess,	
<i>blue solution,</i>	<i>reddish solution.</i>
Treated with alkali carbonates,	
<i>pale green precipitate,</i>	<i>violet red precipitate.</i>

Phosphates. — The presence of the phosphates in mixture with third group salts complicates the analysis from the fact that the phosphates of the fourth group metals can only be held in solution by acids, and hence, when the solution is rendered alkaline by NH_4OH in the third group, Ca, Ba, or Sr, are precipitated. Whether phosphates are present or not may be ascertained by the test with ammonium molybdate (see phosphoric acid). If found to be present, their separation may be studied from a larger work. See Prescott and Johnson, fourth revised edition, article 305.

Synoptical View of the Separation of Third Group Metals.

Condense the foregoing work into a complete synopsis, similar to that on page 40, of the separations in this group.

NOTE: — These synopses will lack clearness and their value be largely destroyed if the attempt is made to exhibit all of the details of the work, confirmatory tests, etc. Only the principal resulting compounds are to be shown. It ought also to be said that these synoptical views will only possess value to the student in proportion as they are the result of his own ingenuity and labor. Such work merely copied from others is almost wholly valueless.

CHAPTER XII.

OCCURRENCE IN NATURE AND USES OF THIRD GROUP METALS.

What metal is of the most importance to man?

In what form is Fe found in nature?

Name the most valuable ores.

For what is iron pyrites valued?

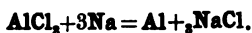
Describe the process of smelting Fe from its ores.

What is steel? How is it made?

What is cast iron? Wrought iron? How are these varieties made? What is meant by the "temper" of steel?

What is malleable iron? Pig iron?

What is the third most plentiful and widely occurring element? How prepared?



What is the probability that it will some time replace iron for many purposes?

What can you say of the hardness of the metal Al? Its malleability? Ductility? Tenacity? Its specific gravity? Its power to conduct electricity? Its tarnishing in the air?

What are some of its prospective uses?

What is alum? For what purpose is it introduced into baking powders? How may you detect its presence?

What is topaz? Beryl? Turquoise? Ruby? Emery? Sapphire? Corundum? Emerald?

What is common clay? Bricks made from some kinds of clay are red. Why?

How does Cr occur in nature? What is the principal

use of the metal? What is chrome alum? Chrome green? Chrome yellow?

Occurrence, properties, and uses of Ni?

What is the composition of our five cent coins? Answer the last question by dissolving a "nickel" in HNO_3 and determining the metals the coin contains.

Occurrence, properties, and uses of Mn?

Study the action of a solution of $\text{K}_2\text{Mn}_2\text{O}_8$ on the organic matter in impure drinking water.

How is Zn found in nature? The most important of its ores? How separated? Its properties and uses?

How is Zn utilized in the laboratory? What are the principal impurities in commercial Zn and how removed? What is galvanized iron?

Heat a small piece of Zn on charcoal with the blowpipe, using the oxidizing flame. The white fumes of zinc oxide, "philosopher's wool," will be seen, and the charcoal will be covered with a film which is yellow while hot, but becomes white when cool.

Repeat the same experiment, using a piece of lead.

CHAPTER XIII.

SEPARATION OF METALS OF FOURTH GROUP.

Perform the work suggested below, recording the results (pre. or no pre.) in the proper spaces.

REAGENTS ADDED	TO SOLUBLE SALTS OF			
	Ba	Ca	Sr	Mg
KOH or NaOH				
NH ₄ OH				
NH ₄ Cl and NH ₄ OH				
Carbonates				
NH ₄ Cl and Carbonates				
Sulphates or H ₂ SO ₄				
(NH ₄) ₂ C ₂ O ₄				
Chromates, K ₂ Cr ₂ O ₇				
Na ₂ HPO ₄				

Questions on the Table Work.

1. What salts are precipitated by KOH ?
2. What salts are precipitated by NH₄OH ?
3. How do Mg salts behave when (NH₄)₂CO₃ is added to them, (a) in dilute solutions of the Mg salts, and (b) in concentrated solutions ?

4. How in both cases when NH_4Cl and $(\text{NH}_4)_2\text{CO}_3$ are added?

It is evident that $(\text{NH}_4)_2\text{CO}_3$ might be used as the group reagent, at least for Ba, Ca, and Sr.

5. What would be the effect on this reagent if the given salt were acid or contained free acid?

6. How could this be avoided?

7. If NH_4OH were added to neutralize any free acid mixed with the salt would this precipitate any member of this group?

As Mg precipitates as a carbonate only in concentrated solutions it is best to prevent its formation as such. This precaution the chemist always takes.

8. How can this be done?

9. How are the fourth group salts affected by the addition of NH_4Cl , NH_4OH and $(\text{NH}_4)_2\text{CO}_3$?

10. How do Mg salts behave when, besides the above reagents (9), Na_2HPO_4 is added?

11. Of the carbonates formed in (9) (filtered and thoroughly washed), which are soluble in HCl , H_2O_2 ?

12. Of the acetates thus formed, which will precipitate with $\text{K}_2\text{Cr}_2\text{O}_7$?

13. Of the remaining acetates, which would be precipitated by CaSO_4 ?

14. Would (13) be any positive test for Ca?

15. Which of the remaining acetates, as in (13), would be precipitated by K_2SO_4 , or dilute H_2SO_4 ?

CaSO_4 is soluble in 400 parts of water; SrSO_4 in 7,000 parts; $(\text{NH}_4)_2\text{C}_2\text{O}_4$ will give a visible precipitate in solutions containing one part of a calcium salt to 21,600 parts of H_2O .

The facts stated above suggest a method of separating Sr and Ca, viz., that when the acetate solution has been treated with K_2SO_4 there still remains enough of the CaSO_4 in solu-

tion to give a test with $(\text{NH}_4)_2\text{C}_2\text{O}_4$. The CaSO_4 solution must first be carefully neutralized with NH_4OH . (Why neutralized? Why neutralized with NH_4OH ?)

Confirmatory Tests.

For Barium. — Sulphuric acid or sulphates precipitate from soluble barium salts, all barium as BaSO_4 , insoluble in water, in dilute acid, and in alcohol. Ammonium oxalate precipitates white barium oxalate, soluble in acids. Ammonium hydroxide reprecipitates it from the acid solution.

If Ba is in mixture with Sr or Ca, the filtrate from the precipitate by $\text{K}_2\text{Cr}_2\text{O}_7$ must be examined for the latter metals, first making sure that the Ba is all removed.

Ba salts are precipitated by soluble phosphates as BaHPO_4 , if the reagent is two thirds metallic, and $\text{Ba}_3(\text{PO}_4)_2$, if the reagent is full metallic. Potassium chromate or dichromate precipitates BaCrO_4 , yellow, but slightly soluble in acetic acid, soluble in HCl .

For Calcium. — Ammonium or potassium oxalate precipitates calcium oxalate, CaC_2O_4 , from dilute solutions of calcium salts, not soluble in acetic but soluble in hydrochloric and nitric acids. If a platinum wire, which has previously been dipped into hydrochloric acid, is moistened with a calcium salt and held in the flame, a yellowish red color will be produced.

For Strontium. — Precipitation of Sr salts by sulphuric acid or sulphate does not constitute a test for this metal if Ba is present with it. A mixture of Ba and Sr salts may be precipitated as carbonates, dissolved as chlorides, the solution evaporated to dryness and the SrCl_2 dissolved out by absolute alcohol. Potassium chromate precipitates SrCrO_4 , yellow, soluble in acetic acid (distinction from Ba). Dichromates (as $\text{K}_2\text{Cr}_2\text{O}_7$) do not precipitate strontium from the acetate solution (distinction from Ba).

Strontium compounds color the flame crimson.

For Magnesium. — The precipitation of Mg salts with NH_4OH and $(\text{NH}_4)_2\text{CO}_3$, and the solubility of the resulting hydroxide and carbonate in NH_4Cl , together with the formation of the phosphate insoluble in NH_4Cl , afford distinctive tests for this metal.

Take the atomic weights of calcium and barium and find their mean. What is it? Can you find other facts by which it may be seen that strontium occupies a position midway between calcium and barium?

Synoptical View of the Separation of Fourth Group Metals.

Make this on the basis of the preceding work. For the method of doing this see page 40 and note on page 56.

CHAPTER XIV.

OCCURRENCE IN NATURE AND USES OF FOURTH GROUP METALS.

How in nature is Ba found?

Character and uses of its compounds?

Is metallic Ca found in nature?

What is limestone? Marble? Chalk?

What is the composition of egg shells, clam shells, and corals? Of bones?

What is quicklime? From what is it prepared and how?

What is slacked lime? Mortar? "Putty coat" or "hard finish"? (Ask some practical mason.)

What is water lime? Lime water?

What is bleaching powder? How is it used?

What is gypsum? Plaster of Paris? Land plaster?

Drive out the water of crystallization from a small amount of gypsum by carefully heating it in a porcelain evaporating dish. Powder the residue, and make it into a paste with water. Allow it to stand, and explain the results.

What is the most frequent ingredient of "hard" water? When will boiling make hard water soft?

What is the reaction between hard water and soap?

Cases of chemical action are constantly occurring in everyday life, and it should be the habit of the student of chemistry to recognize these, and be able to explain them. An illustration of this thought is found in the difficulty experienced when we attempt to wash with soap and hard water. Soap is

a salt of potassium or sodium, and easily soluble in water. When, however, the water contains calcium carbonate or sulphate a reaction takes place and an *insoluble* calcium stearate occurs, thus, —

Sodium stearate + calcium carbonate = calcium stearate + sodium carbonate.

Tell the story of the stalactite.

What is fluor spar? Iceland spar?

Occurrence of Sr? Compounds and uses?

Prepare carefully a small amount of one or two forms of colored fires for tableaux and pyrotechnics. For red fire, mix equal parts of finely powdered $\text{Sr}(\text{NO}_3)_2$ and KClO_3 with an equal bulk of pulverized shellac. Powder each substance separately and mix carefully. For a green fire use $\text{Ba}(\text{NO}_3)_2$ in place of the strontium nitrate.

Occurrence of Mg?

Properties and uses of the metal? Hold a piece of Mg ribbon in the forceps and heat it in the flame.

What is magnesia? Epsom salts? Magnesite?

What is meerschäum?

CHAPTER XV.

SEPARATION OF THE METALS OF FIFTH GROUP.

What metals are precipitated by $(\text{NH}_4)_2\text{CO}_3$?

What metals are precipitated by KOH or NaOH?

What metals remain to constitute a fifth group?

Of these, which are precipitated by $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$?

Which by $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ and $\text{C}_2\text{H}_5\text{OH}$?

Note which of the metals of the Fifth Group impart a characteristic color to the flame when a Pt wire is moistened in a salt of each and held in the colorless alcohol or Bunsen flame. Study these flames as seen through blue glass. The best result will be obtained if the wire is first moistened in HCl and then in the salt to be tested.

Note the odor given off when KOH is mixed with an ammonium salt and gently warmed. Test the gas given off with a moistened red litmus paper.

Note the easy and thorough evaporation of ammonium compounds when a drop is placed on the platinum foil and gently heated.

For contrast to this, evaporate in the same way, CaCl_2 , or $\text{K}_2\text{Cr}_2\text{O}_7$, or MnCl_2 .

Rinse a beaker glass with ammonia and a second one with hydrochloric acid, keeping them separated by covering each with a piece of paper. Now bring the mouths of the beakers together and withdraw the papers. Explain the result.

The metal lithium, Li, occurs in nature in small quantities but is quite widely distributed, being found in the ashes of many plants, notably in that of tobacco and the beet. It is

the lightest of the metals; it melts at 180° , and burns with an intense white light.

Lithium compounds color the flame a beautiful red.

The phosphate and carbonate of lithium are but sparingly soluble in water and hence may be precipitated from concentrated solutions of lithium salts.

From the above study of these metals may be devised a method of separation of the metals of the fifth group.

CHAPTER XVI.

OCCURRENCE IN NATURE AND USES OF FIFTH GROUP METALS.

Drop a bit of metallic Na or K into a dish of water and ask yourself whether these metals could possibly exist in a free state.

What is rock salt? What is common salt? Where found and how prepared for use? What other compounds are associated with salt in sea water?

Moisten some wood ashes with HCl and examine the flame. Dissolve wood ashes in water, filter and concentrate the solution, and treat with tartaric acid. Treat the concentrated solution with HCl and test the gas given off.

Describe and explain the chemistry of the old-fashioned "leach tub."

What is lye? Hard soap? Soft soap? How made?

Burn some hard soap to an ash, moisten with HCl, and study the flame reaction.

What is gunpowder? Dynamite?

Take a piece of ordinary phosphorus as large as a pin's head, and sufficient finely pulverized potassium chlorate to cover it. Fold the mixture closely in a piece of writing paper, place upon an anvil, and strike it a sharp blow with a hammer. Use small quantities.

Rub together in a mortar small quantities of potassium chlorate and flowers of sulphur, keeping the hand protected with a glove, and holding the mouth of the mortar away from the face.

Fill a small Erlenmeyer flask with water and place in the

bottom some very small pieces of phosphorus and a few crystals of potassium chlorate. With a thistle tube direct a few drops of strong H_2SO_4 upon the chlorate. Presently the phosphorus takes fire, and burns brightly under the water.

What is saltpetre? Glauber's salt?

What is saleratus? How made? Soda? Sal ammoniac? Saliva?

What is borax? Why used by the blacksmith? Why by the barber? Does borax soften hard water? Try it.

What is caustic soda? Caustic potash?

Pulverize a little window glass, moisten with HCl and test for flame reaction. Do the same with a broken test tube and see if there is a difference between the two.

What is common alum?

How is oxygen obtained from potassium chlorate?

From what is "laughing gas" obtained?

CHAPTER XVII.

PERIODIC LAW OF THE ELEMENTS.

The famous generalization, known as the periodic law of the elements, possesses great interest after the student has passed over the work of grouping and separating the metals. A preliminary study of the subject may be made, as suggested below, but the fuller treatment must be looked for in larger works.

1. Arrange the elements in the order of their atomic weights from the one having the least to the one having the greatest.

2. Ignoring H (why?) and beginning with the next in the scale, rearrange the elements, as they appear in (1), in horizontal series.

(a) In the first series place the first seven elements.

(b) In the second series, the next seven elements, placing the eighth under the first, the ninth under the second, etc.

(c) In the third series put ten elements, placing the fifteenth under the eighth, the sixteenth under the ninth, and so on.

(d) In the fourth series put six elements, the twenty-fifth under the fifteenth, and so on, but leaving the twenty-eighth blank.

(e) In the fifth series put ten elements, the thirty-second under the twenty-fifth and leaving the thirty-eighth blank.

(f) The sixth series consists of the seven elements beginning with Ag.

(g) In the seventh series will occur, as the first three elements, Cs, Ba, La.

3. Now notice that the valency of the elements of the first series begins with one, increases to a maximum and decreases to one. Is this generally true of all the series?

4. Adapt the proper specific gravities to the second series and notice whether a law similar to that in (3) can be observed. Is this true of other series?

5. What group of metals is found in the first *vertical* column? What in the second? What group of non-metals is found in the seventh vertical column?

6. Could the atomic weight, valency, and specific gravity of the element which will (when found) fill the blank place in the fourth series be approximately determined?

These and many other facts are summed up in the statement that *the properties of the elements* and their compounds present themselves as *periodic functions of the atomic weights*.

Consult Encyclopædia Britannica, Vol. V, p. 543; Smith's Richter's Inorganic Chemistry, p. 241; Roscoe and Schorlemmer's Treatise on Chemistry, Vol. II, Pt. II, p. 506; or any late work on general chemistry.

CHAPTER XVIII.

UNKNOWN.

In order to insure clearness in the practical use of the methods for the identification and separation of metals which have been formulated from the preceding work, a few suggestions will here be given in the way of recapitulation of those methods.

1. If the substance, the composition of which it is desired to know, is in the solid state, it is dissolved by some of the methods given in Chapter IV.

2. A small portion of the solution is treated with HCl, and, in case a precipitate results, enough of the solution is used to precipitate a sufficient quantity for the work of separation in first group.

Enough HCl must be used to completely precipitate the first group metals, if it is suspected that other groups are present. Why?

The precipitate is filtered, washed (why?) and treated with hot water and NH_4OH . See Chapter VII.

3. The filtrate from Group I (if first group be present), or the original substance, is treated with $\text{HCl} + \text{H}_2\text{S}$. A precipitate shows the presence of second group metals, and these will be examined according to Chapter IX.

4. The filtrate from Group II, freed from HCl and H_2S by boiling (if Group II be present), or (if Group I or II be not present) *the original solution*, is now treated with HNO_3 (to oxidize ferrosium), NH_4Cl (why?), and NH_4OH . A precipitate indicates the presence of Fe, Cr, or Al. These will be examined by the methods in Chapter XI.

5. The filtrate from (4), or, if Fe, Cr, or Al be not present,

the solution, already treated with NH_4Cl and NH_4OH , is tested with $(\text{NH}_4)_2\text{S}$, a resulting precipitate indicating that the solution contains Mn, Zn, Co, or Ni. These will be separated by the methods in Chapter XI.

6. If metals of any of the preceding groups be present, the filtrate must be used for work in the following groups. The filtrate from Group III, or the original substance, is now tested with NH_4Cl (why?), NH_4OH (why?), and $(\text{NH}_4)_2\text{CO}_3$. The precipitate is washed on the filter, dissolved with acetic acid, and examined for Ba, Ca, and Sr. Chapter XIII.

7. After sufficient $(\text{NH}_4)_2\text{CO}_3$ has been used to completely precipitate Ba, Ca, and Sr, the filtrate from these precipitates may be examined for Mg by the reagent Na_2HPO_4 .

8. The original substance is examined for Fifth Group metals, precipitation by $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ for NH_4 and K; the odor test for NH_3 , and the flame test for K, Na, and Li. Chapter XV.

9. The metal having been found, the acid is next looked for by methods in Chapter XIX.

Mixtures.

The analysis must be guarded at certain points when a mixture of several substances is to be examined. In the first place, there must be *complete precipitation and separation* of the metals of one group, or one division of a group, before the filtrate can be examined for other metals. This arises from the fact that the salt of any metal will precipitate with the reagents of all the groups succeeding the one in which it belongs, and hence false indications will be gained unless complete separation of one metal is made before search is made for another.

Again, complications will arise if mixtures of dry salts are to be examined. The chief difficulty in such cases will arise in getting the substance into solution. A little thoughtfulness will enable the student to guard against any possible cases. For example, the substance may be a mixture of

(a) Two salts, both of which are soluble in water and such as will not react on each other when dissolved. Ferrous sulphate and manganous chloride.

(b) Two salts, both of which are soluble in water but which will react on each other as soon as dissolved, forming one salt that is insoluble. Lead acetate and manganese chloride.

(c) Two salts, one soluble in water and the other insoluble. Calcium carbonate and potassium nitrate.

(d) Two salts, both insoluble in water, both soluble in HCl; or, one soluble in HCl, the other not, etc.

It will be profitable for the student to extend this list of possible cases.

CHAPTER XIX.

ACIDS.

The work thus far has had for its end the detection and recognition of the metals. It has been no part of the work to inquire what acids have been combined with these metals only so far as the known composition of the reagents used have made these apparent.

The Grouping of the Acids.

As in the metals, the acids may be thrown into provisional groups according to their behavior with certain reagents.

The following scheme suggests a classification of the acids, the reagents to be used, and the order in which the steps are to be taken :—

GROUP I—Group reagent, $\text{Ba}(\text{NO}_3)_2$, causing precipitation from *neutral* solutions of the salts of

H_2CrO_4
 H_2AsO_4
 H_2SO_4
 H_3PO_4
 H_2BO_3
 $\text{H}_2\text{C}_2\text{O}_4$
 HF
 HIO_3
 H_2CO_3
 H_2SiF_6
 H_2SO_3
 H_4SiO_4
 $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$

GROUP II—Group reagent, AgNO_3 , and not precipitated by $\text{Ba}(\text{NO}_3)_2$ in solutions of salts of

HCl
 HBr
 HI
 HCN
 $\text{H}_3\text{FeC}_6\text{N}_6$
 $\text{H}_4\text{FeC}_6\text{N}_6$
 H_2S
 HClO
 HClO_2
 HCNS
 H_3AsO_3

GROUP III—Salts of acids not precipitated by $\text{Ba}(\text{NO}_3)_2$ or AgNO_3 .

HNO_3
 HNO_2^*
 HClO_3
 HBrO_3^*
 $\text{HC}_2\text{H}_3\text{O}_2$
 HClO_4
 H_2MnO_4^*

GROUP IV—Organic acids, which carbonize on heating.

$\text{HC}_3\text{H}_5\text{O}_2$
 $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$

* May precipitate with silver nitrate if the solution is concentrated.

Notes and Queries.

For a brief course in Qualitative Analysis, only the acids given on the list on page 12 may be studied.

The salt of any acid will give the test of that acid.

The presence of one acid will generally not interfere with the detection of others; so that the different acids of which a mixture is composed may be tested for in separate portions of the original substance.

Metals should generally be determined before search is made for the acids, as the work for the former often gives indication of the presence of some special acid; or the evidence may make it possible to exclude from consideration one or more groups of acids. For example, if the substance under examination is soluble in water and contains Ba, none of the first group of acids can possibly be present. Why?

Which of the acids of Group I contain elements which would be detected in the examination for metals?

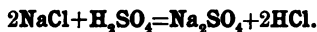
Of the salts of barium formed by the first group of acids, BaSO_4 and BaSiF_6 are insoluble in HCl , all others soluble.

How many of the first group of acids will precipitate with AgNO_3 ? When will this fact complicate the analysis?

Further Examination of Salts for Acids.

The work suggested in the table and the pages which follow should be done by the student in the laboratory, with known substances, the equations should be written for reactions, and the results recorded in the permanent notebook.

Many acids are separated from their salts by H_2SO_4 , and when thus set free may often be detected by their characteristic odor or color. Thus, when a chloride, as NaCl , is treated with H_2SO_4 , hydrochloric acid is given off and may be recognized by its sharp and penetrating odor.



The Method. — Strong sulphuric acid is added to the salt to be tested (the latter in the solid form, or, at least, in a concentrated solution), the solution gently warmed, and the following results looked for :

SALTS.	ODOR.	COLOR.	REMARKS.
Acetates, Arsenates, Arsenites, Borates, Bromates, Bromides, Carbonates, Chlorates, Chlorides, Chromates, Cyanides, Ferro-cyanides, Ferri-cyanides, Fluorides, Hypochlorites, Hyposulphites, Iodates, Iodides, Nitrates,	Vinegar, Odor of Cl, Acrid, None, Odor of Cl, Penetrating, None, Peach Blossom, " " " " Poisonous, Odor of Cl,	Colorless. Brown. Brown. Colorless. Yellow. Colorless. Colorless. Colorless. Colorless. Colorless. Colorless. Colorless. Greenish.	No escape of gas. No escape of gas. No escape of gas. Sudden effervescence. Detonates. See Thiosulphates. No escape of gas.
Nitrites, Oxalates, Phosphates, Silicates, Sulphates, Sulphites, Sulphides, Tartrates, Thiosulphates,	Irritating, Sometimes ni- trous fumes, Irritating, None, Burning S, Rotten Eggs, SO ₂ , CO ₂ , CO, SO ₂ ,	Violet. Colorless. Red. Colorless. Colorless. Colorless. Colorless. Colorless.	No escape of gas. No escape of gas. No escape of gas.

Confirmatory Tests.

After the preliminary tests have been made as above, any indication there obtained may be confirmed by making special tests for the acids as follows :

For Acetic Acid, $HC_2H_3O_2$, in Acetates. — Sulphuric acid, applied to a solid or concentrated solution of an acetate, separates acetic acid, which may be recognized by the well-known *vinegar odor*. If alcohol be added to the same solution, "acetic ether," or ethyl acetate, $C_2H_5C_2H_3O_2$, will be formed and recognized by its fragrant odor.

Acetates treated with FeCl_3 give a *red solution* of ferric acetate. Compare this solution with the blood-red solution of ferric sulphocyanide.

Arsenates and Arsenites.—These will be determined in connection with the work in the second group of metals.

For Boric Acid in Borates.—The element boron, B, forms but one oxide, boracic anhydride, B_2O_3 , and the corresponding acid is orthoboric acid, H_3BO_3 . By heating this to the boiling temperature, orthoboric acid is converted into metaboric acid, HBO_2 .

The common commercial salt is "borax" or sodium biborate, $\text{Na}_2\text{B}_4\text{O}_7$, $(\text{NaBO}_2)_2\text{B}_2\text{O}_3$.

The common test for a borate is conducted as follows: If a borate is moistened with H_2SO_4 in an evaporating dish, and alcohol added, on igniting the latter a *green flame* is produced. Copper interferes with this test, and if present should be removed by H_2S and the test for a borate made in the filtrate.

For Bromic Acid, HBrO_3 , in Bromates.—All the bromates are soluble in water, except Ag, Pb, and $(\text{Hg})_2$, which are sparingly soluble. Silver nitrate precipitates, from concentrated solutions, silver bromate, AgBrO_3 , white, soluble in NH_4OH . Hydrochloric acid separates bromine from this precipitate which will color carbon disulphide yellow. Compare AgBr.

For Hydrobromic and Hydriodic Acids, HBr and HI , in Bromides and Iodides.—Make a thin paste by heating a small portion of starch in water in a test tube. Add the solution to be tested. Now add to the mixture, drop by drop, chlorine water. A *yellow color* will be produced by bromine, and an *indigo blue* by iodine.



The chlorine water may be made by covering a minute particle of KClO_3 with HCl and heating. When the chlorine fumes are liberated freely, dissolve them in water, thus forming a green solution.

Carbon disulphide, CS_2 , may be used in place of the starch, in which case the iodine gives a *violet red color*, and the bromine a *yellow or reddish yellow*.

For Carbon Dioxide, CO_2 , in Carbonates. — Treat a carbonate with H_2SO_4 in a test tube and quickly bring the mouth of the tube to that of another containing $\text{Ca}(\text{OH})_2$ solution, allowing the CO_2 to pass from the first tube into the second, finally shaking the latter so as to mingle the gas with the lime solution. A *white precipitate* of CaCO_3 will be formed.

With a piece of glass tubing, pass air from the lungs into clear lime water and note the result. What is “choke damp”?

For Chloric Acid, HClO_3 , in Chlorates. — The *greenish yellow gas* and the *detonation*, caused by treating a chlorate with H_2SO_4 and warming, are sufficient for the determination of this acid.

Use small quantities of the chlorate and keep the test tube pointed away from the face.

Take a small quantity of dry KClO_3 , divide in two portions. Dissolve one in water and add AgNO_3 . Heat the other to redness in a test tube or crucible, dissolve the residue in water and add AgNO_3 . Explain the difference of the two results.

For Hydrochloric Acid, HCl , in Chlorides. — Only the chlorides of the first group of metals are insoluble in water. This statement is only true for normal chlorides as some *basic chlorides* are insoluble in water. Consult some larger work.

Hydrochloric acid is a gas at ordinary temperatures, and, if a glass rod wet with AgNO_3 be held at the mouth of a test tube in which a chloride has been treated with H_2SO_4 , a *white precipitate* of AgCl will be formed *on the rod*. This precipitate will readily dissolve in NH_4OH and reprecipitate by acidulating with HNO_3 .

Any soluble chloride added to a solution of a lead salt will precipitate lead chloride, soluble in hot water.

Any chloride with H_2SO_4 and MnO_2 will give Cl.

For Chromic Acid, H_2CrO_4 , in Chromates. — Lead salts precipitate, from solutions of chromates, lead chromate, PbCrO_4 , "*chrome yellow*." Barium salts precipitate barium chromate, BaCrO_4 , *yellowish white*. Silver salts yield a *dark red* silver chromate, Ag_2CrO_4 . Mercurous nitrate precipitates mercurous chromate, Hg_2CrO_4 , *orange red*.

For Hydrocyanic Acid, HCN , in Cyanides. — Hydrocyanic acid having been set free by H_2SO_4 will precipitate AgCN from silver nitrate on a glass rod. The silver cyanide possesses the same solubilities as silver chloride, and hence arises the necessity for some additional test to distinguish between them, viz.,

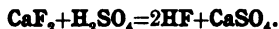
A cyanide may be changed to a sulphocyanide as follows: To a portion of the material, supposed to be a cyanide, in an evaporating dish, add a few drops of $(\text{NH}_4)_2\text{S}$ and warm until the excess of sulphide is all driven off. Add HCl to acid reaction and test the solution with FeCl_3 . *A blood red solution* indicates that the original substance was a cyanide. The red solution should decolor with HgCl_2 .

For Ferro- and Ferricyanides.

REAGENTS ADDED TO	FERROCYANIDES	FERRICYANIDES
Bismuth salts	Greenish white pre.	Light brown pre.
Copper salts	Red brown pre.	Olive green pre.
Ferrous salts	Whitish blue pre.	Blue pre.
Ferric salts	Prussian blue pre.	Green solution.
Silver salts	White pre.	Red brown pre.

For Hydrofluoric Acid, HF , in Fluorides. — Mix the solid fluoride with solid acid potassium sulphate, KHSO_4 . Dip in the mixture a borax bead formed on a platinum wire and test in the Bunsen or alcohol flame. *A green flame* appearing only for an instant indicates the formation of BF_3 . Confirm by the "etching" test: The glass which is to be etched is covered with a thin coating of wax and through this the design is drawn. The glass is now placed over a leaden dish in which calcium fluoride,

CaF_2 , has been placed. The mixture is gently warmed, until chemical action commences, and then is to be left for several hours.



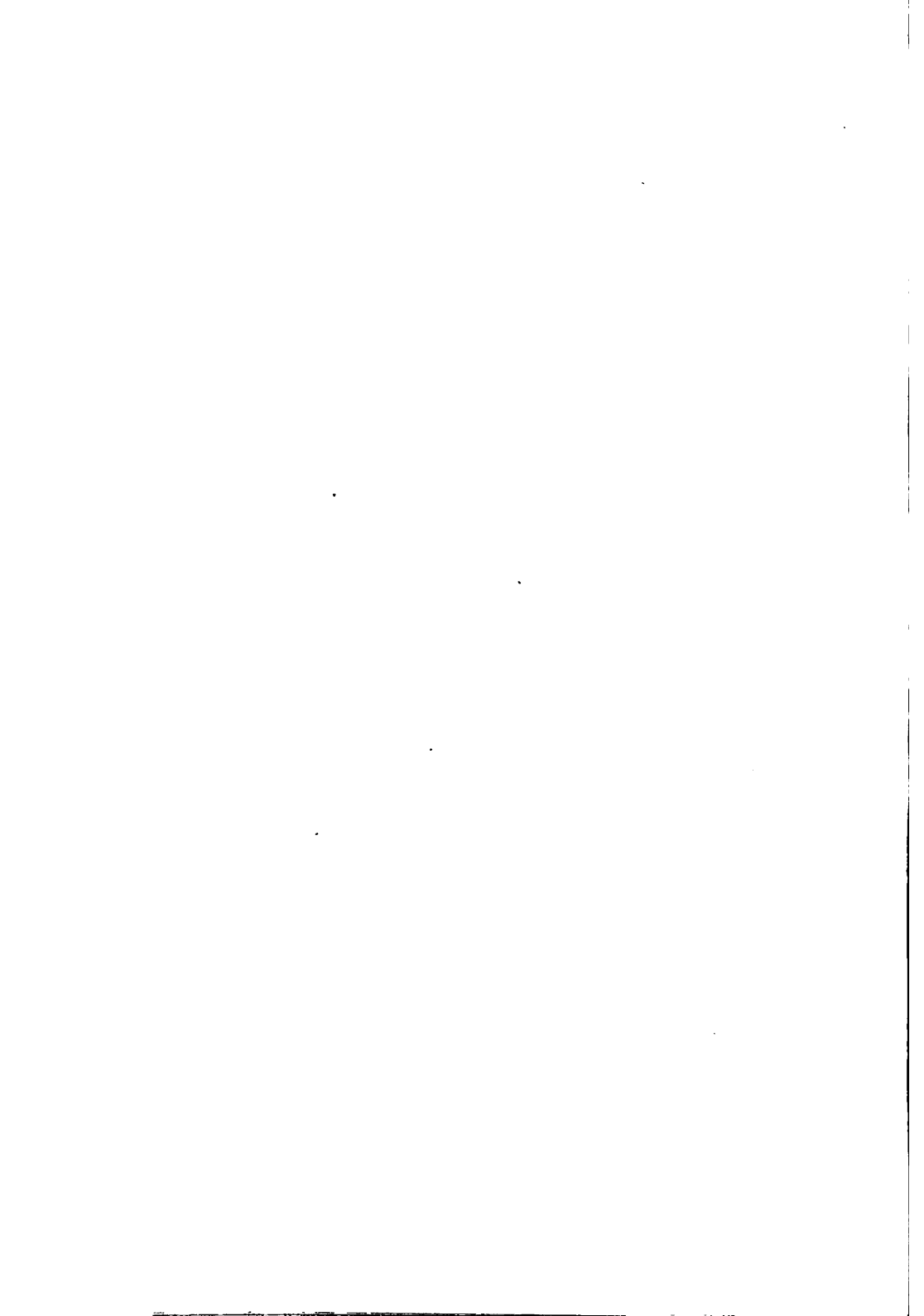
For Iodic Acid, HIO_3 , in Iodates. — Consult some larger work.

For Nitric Acid, HNO_3 , in Nitrates. — All normal nitrates are soluble in water. The "*brown ring*" test is as follows: Take in a test tube a small quantity of H_2SO_4 ; incline the test tube and pour an equal amount of ferrous sulphate in such a way that the two liquids do not mix. Cool, and drop into the mixture the substance to be tested. If a nitrate is present, the FeSO_4 reduces the HNO_3 to NO , and this, dissolving in the excess of FeSO_4 , forms a ring of dark brown liquid in the layer between the two liquids.

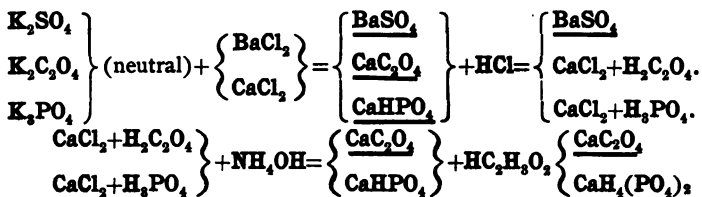
The formula for the brown ring is $(\text{FeSO}_4)_2\text{NO}$; let the student write the equations for the successive steps of the process and finally the equation for the complete test. As preparatory to this, notice that free nitric acid, HNO_3 , gives the brown ring without the aid of the H_2SO_4 . Then why is the H_2SO_4 used? What is the initial movement? When does it take place? The ferrous sulphate has been oxidized to ferric sulphate. How many molecules of ferrous sulphate are needed for one molecule of ferric sulphate? What else is needed? From what source is this derived? What has been the change produced in the H_2SO_4 ? By what was this change produced? How much O has been liberated? How much H_2SO_4 can this decompose? How much FeSO_4 can this oxidize? etc.

How will an iodide behave when examined by this test?

For Nitrous Acid, HNO_2 , in Nitrites. — The same test may be made as for nitrates, with the difference that the evolution of the *nitrous fumes* is much more abundant. Acetic acid may be used in place of H_2SO_4 and this makes a distinction between nitrates and nitrites.



For Sulphuric, Oxalic, and Phosphoric Acids, in Sulphates, Oxalates and Phosphates. — Using the potassium salts of these acids as types, the method of testing may be summarized as follows: —

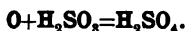


Test the solution of the phosphate with ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4$. A *yellow precipitate*, after warming, is indication of a phosphate.

For Silicic Acid, in Silicates. — If a bead formed on a platinum wire with “microcosmic salt,” $\text{NaNH}_4\text{HPO}_4$, be dipped in a powdered silicate and intensely heated, small *spicules of silica* will be seen floating in the fused bead. This test may serve for the detection of silicates.

Only potassium and sodium silicates are soluble in water. Other silicates are made soluble by first fusing them on the platinum foil with a mixture of Na and K carbonates, or by boiling in a solution of KOH or NaOH.

For Sulphurous Acid, H_2SO_3 , in Sulphites. — The sulphites of the metals of the alkalis are soluble in water, all others insoluble; hence, solutions of sulphites are precipitated by the soluble salts of all metals not alkali. Sulphurous acid and sulphites are active reducing agents,



Test the last statement by reducing ferric salts and potassium permanganate.

For Hydrosulphuric Acid, H_2S , in Sulphides. — Sulphides, treated with HCl or H_2SO_4 , evolve H_2S which may be recognized by *its odor* and by blackening paper wet with lead acetate.

CHAPTER XX.

SOME DRY PROCESSES.

The work thus far has been carried on by processes known as "the wet way." Oftentimes the *dry* solid may profitably be examined either as preliminary to the regular examination or as confirmatory to the results there reached.

Flame Tests.

A platinum wire is moistened in HCl and dipped into the solid, or concentrated solution, and held in the flame. Characteristic colors are imparted to the flame:—

Yellow indicates Na (obscured by blue glass).

Violet indicates K (obscured by the yellow of Na, if that metal is present).

Crimson indicates Sr.

Red indicates Ca, Li.

Greenish white indicates Zn.

Green indicates HCl, H_3BO_3 , Ba salts, Cu salts (except the chloride).

Blue indicates $CuCl_2$, Pb, As, Sb.

On Charcoal.

The powdered substance is placed on charcoal, either by itself or mixed with Na_2CO_3 , and heated with the blow pipe, reducing flame. Characteristic coatings are given to the charcoal:

White and volatile, Sb or As. (The latter gives a garlic odor.)

Yellow while hot, white when cold, Sn, Zn.

Yellow while hot, yellow when cold, Pb, Bi.

Brown, Cd.

The following metals yield metallic globules when heated on charcoal with Na_2CO_3 :

Malleable beads, Au, Cu, Ag, Pb, Sn.

Brittle beads, Sb, Bi.

Magnetic particles, Fe, Co, Ni.

Borax Bead.

A clear bead is obtained by fusing borax on a loop of platinum wire ; a very little of the solid substance to be examined is placed upon it, and the whole fused thoroughly in the oxidizing flame.

Colored beads are obtained which, when cold, are as follows :

Blue, Co or Cu (the latter red in R. F.).

Green, Cr ; **light yellow**, Bi.

Light yellow (in R. F. *green*), Fe.

Reddish brown (in R. F. *gray*), Ni.

Amethyst red (in R. F. *colorless*), Mn.

Care of Platinum Vessels.

“Platinum vessels are sometimes considered indestructible, but they are not so, in fact, they *are very delicate* and need to be handled with care.

The *life* of a Platinum crucible depends upon whether it be of *pure* Platinum, and upon the *treatment* it receives ; therefore, always observe the following rules :

1. *Keep it in shape* ; do not bend it ; provide proper receptacle (wood block or plaster cast, with a wooden plug for the inside, fitting the crucible exactly).

2. *Keep it* always perfectly *bright* and *clean*, which can best be done by means of fine (round, not sharp) sea sand, by moistening the finger, dipping it into the sand, and rubbing the crucible till bright. Sometimes HCl will remove stains quickly, but in other cases fusions with Na_2CO_3 , borax, or KHSO_4 are

required for cleansing, and to avoid too much rubbing. *Clean it after each and every use.*

3. Apply heat with care ; *do not heat too quickly* or cracking, due to sudden expansion, will occur. *Do not cool too quickly* ; a cold blast turned on when the metal is at a white heat will cause the metal to crack.

4. *Apply the outer oxidizing flame* ; do not have the inner (reducing) flame touch it, or a gray film will form (showing irregular surface under the magnifying glass).

5. *Always use a bright platinum, or pipe stem, triangle* to rest the crucible on.

6. *Test unknown material before fusing* in the crucible. If no time for analysis is given, heat a sample of the material between a piece of folded up platinum foil and note the action.

7. *Never fuse nor heat in it* the following : free metals ; easily reduced metallic oxides ; the salts of the *heavy metals* (such as lead, tin, bismuth, antimony, etc.), especially their organic compounds.

8. *Phosphoric acids* in some phosphates, in *presence of organic substances*, render the platinum very brittle at high temperatures.

9. Other substances injurious to platinum, under certain conditions, are substances evolving free chlorine, sodium and potassium nitrates, some cyanides and sulphides of metals.

10. Contact with burning charcoal and highly carburetted flames should be avoided."



INDEX.

- ACETIC ACID, 74, 76.
Acids, classification of, 12, 74.
 list of, 12.
 tests for, 74, 81.
Acid radical, 12.
Aluminum, 34, 35, 57.
Ammonium, 65.
Antidote for arsenical poisoning, 49.
Antimony, 43, 45, 46.
Apparatus, 19.
Aqua regia, 23.
Arsenic, 43, 44, 45, 49, 74, 76, 77.
Ashes, 67.
Atomic weights, table of, 9.
BARIUM, 60, 61.
Books, reference, 21.
Borax bead, 83.
Boric acid, 74, 76, 77.
Bromic acid, 74, 76, 77.
CALCIUM, 60, 61.
Carbonic acid, 74, 76, 78.
Carbon dioxide, 78.
Charcoal, tests on, 82.
Chemical action, 8.
 affinity, 8.
 compound, 8.
Chloric acid, 74, 76, 78.
Chlorine, 23.
Chromic acid, 74, 76, 79.
Chromium, 54, 55.
ELEMENTS, table of, 9.
 periodic law of, 69.
Equation, 26, 27.
Evaporation, 24.
Exchangeable hydrogen, 12.
FLAME TESTS, 82.
Formulas, how named, 14.
GLASS, 68.
Gold, 50.
Greek fire, 64.
HYDRACIDS, 12.
Hydrobromic acid, 74, 76, 77.
Hydrochloric acid, 74, 76, 78.
Hydrocyanic acid, 74, 76, 79.
Hydriodic acid, 74, 76, 77.
Hydroferricyanic acid, 74, 76, 79.
Hydroferrocyanic acid, 74, 76, 79.
Hydrofluoric acid, 74, 76, 79.
Hydrosulphuric acid, 74, 76, 81.
IODIC ACID, 74, 76, 80.
Iron, 53, 54, 55.
LABORATORY, 16.
Laboratory methods, 1-6.
Lead, 38, 39.
MAGNESIUM, 60-62.
Manganese, 55.
Marsh's test, 44.
Mercury, 38, 39, 48.
Metal, 8.
Metals, grouping of, 32.
Method, the true, 2.
Mixtures, 72.
NEUTRALIZATION, 13.
Nickel, 56.
Nitric acid, 53, 74, 76, 80.
Nitro-hydrochloric acid, 23.
Nitrous acid, 74, 76, 80.
Nomenclature of acids, 12.
 of salts, 13.
Non-metal, 8.
Note-book, how kept, 6, 30.
OXACIDS, 12.
Oxalic acid, 74, 76, 81.
Oxidation, 52, 53.
PERIODIC law of elements, 69.
Phosphates, 56.
Platinum vessels, 84.
Precipitation, 24.
Program, daily, 3.
REAGENTS, 18.
 cost of, 20.
Reducing agents, 53.
SALTS, classification of, 13.
Separation of first group metals, 38.
 of second group metals, 43.
 of third group metals, 51.
 of fourth group metals, 59.
 of fifth group metals, 65.
Silicic acid, 74, 76, 81.
Silver, 38, 39.
Soap, 63.
Solubility, 22.
Solubilities, table of, 31.
Solution, chemical, 23.
 physical, 22.
 physico-chemical, 24.
Solvents, 23.
Strontium, 60, 61.
Student in laboratory, 4.
Sulphuric acid, 74, 76, 81.
Sulphurous acid, 74, 76, 81.
TIME required, 3.
Tin, 43, 44, 45.
Unknowns, 71.
Valence of elements, 9.
Zinc, 55.

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